# SOURCE-RECEPTOR RECONCILIATION OF SOUTH COAST AIR BASIN PARTICULATE AIR QUALITY DATA

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## ABSTRACT

Chemical element balance and chemical tracer techniques are used to identify the source types contributing to particulate air quality in the South Coast Air Basin. An inventory of fine particle trace metals emissions in that air basin is constructed for the year 1976. It is shown that over 80% of the fine lead emissions come from highway traffic, 81% of the nickel arises from fuel oil fly ash, and more than 90% of the iron and manganese comes from soil-like materials. Then, using these metals as tracers for their most prominent source types, the ambient aerosol burden at 10 air monitoring sites is subdivided into contributions from particular source types. It is found that most monitoring sites are exposed to aerosol containing about 20% highway vehicle exhaust, 1% to 2% fuel oil fly ash, 20% to 50% soil dust or road dust, with sulfates and nitrates each present at about 15% of total mass. Source assessments based on currently available trace metals air monitoring data can be constructed and used to improve the accuracy of particulate emission control stategies.

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# CHAPTER 1

## INTRODUCTION

Trace element concentrations in airborne particulate matter have been measured routinely at hundreds of locations in the United States by state and local air pollution control agencies and by the National Air Surveillance Network (NASN). Some of the NASN data were acquired beginning over 20 years ago, while some state and local agency data now extend over more than a ten year period. Yet in spite of the tremendous spatial and temporal coverage of these data sets, relatively little use has been made of them in an attempt to assist quantitative aerosol source apportionment for pollution abatement planning. The purpose of this report is to demonstrate that the major sources contributing to particulate air quality at a monitoring site can be identified on the basis of the historical routine air monitoring data base. The quantities of soil dust, fuel oil fly ash, motor vehicle-generated aerosol, sulfate compounds and nitrate compounds present in the atmosphere in selected locations in southern California will be estimated.

Hidy and Friedlander (1970), Miller et al. (1972), and Friedlander (1973) have shown that the characteristic chemical element signatures of specific emission sources can be used to trace the relative contribution of each source type to the particulate matter measured in an ambient aerosol. Their method consists of an element by element source-receptor chemical balance performed on the ambient sample.

Assume that chemical element emissions from each source are averaged over the particle size spectrum, and that each source type emits a

characteristic pattern of chemical elements or compounds in constant proportions. Then the mass concentration, $c_i$, of each element $i = 1,2,\ldots,n$ in an ambient sample can be related to the aerosol sources by the expression

$$c_i = \sum_j f_{ij} a_{ij} S_j \qquad (1)$$

where $a_{ij}$ is the percentage of chemical species i in the particulate emissions from source j, $S_j$ is the mass concentration of material from source j observed at the receptor site, and $f_{ij}$ is the coefficient of fractionation, representing the fraction of species i from source j that appears at the sampling site (fractionation is often neglected). Thus if the chemical composition of the emissions from the major particulate sources is known, along with the chemical composition of an ambient sample, equation (1) defines a series of simultaneous relationships that may be solved for the relative mass contributions, $S_j$, of the various sources to the ambient sample.

Chemical element balance or tracer techniques have been demonstrated in the Los Angeles area (Miller et al., 1972; Friedlander, 1973; Gartrell and Friedlander, 1975; Hammerele and Pierson, 1975), New York City (Kniep et al., 1972; Kleinman et al., 1980), Chicago (Gatz, 1975), Washington D.C. (Kowalczyk et al., 1978) and in Portland, Oregon (Watson, 1979). Additional work is reviewed by Cooper and Watson (1980) and by Gordon (1980). In most of these studies, ambient measurements on circa 20 chemical elements or compounds were acquired from an air monitoring program designed to meet the specifications of such a

material balance. Data reduction procedures vary from one study to the next. Typically, key marker elements like aluminium and silicon are measured as soil dust tracers, lead and bromine are measured to indicate the presence of leaded auto exhaust, and sodium would be measured a sea salt tracer. Then the ambient chemical data on perhaps eight marker elements are matched to a linear combination of five or six major source types by a weighted least squares fitting procedure. Once the source contributions, $S_j$, to the ambient samples have been determined, the contribution of those sources to chemical elements not included in the least squares fitting procedure can be examined to check the accuracy of the chemical element balance (see Kowalczyk et al., 1978).

A major deterrent to the application of chemical element balance techniques to historical pollution control agency air monitoring data sets lies in the fact that the historical monitoring programs were not designed with a chemical element balance in mind. The number of chemical elements measured often is small, and key marker elements such as aluminum or silicon for soil dust usually are unmeasured.

The objective of this research is to develop techniques that relate source contributions to ambient particulate air quality using data characteristic of historical routine air quality monitoring programs. The approach taken is to employ emissions inventory data to assess the ability of those elements that were measured to serve as tracers for major source types. Then source contribution assignments will be obtained from a variety of alternative chemical element balance

and chemical tracer calculation procedures. Chemical element balance results will be checked against multivariate statistical methods that take advantage of the time series nature of the ambient data and the tremendous numbers of ambient samples available. Methods developed will be tested on both local agency and NASN data taken in the Los Angeles area to determine if source assignments obtained using data from different monitoring networks still converge on a common answer.

# CHAPTER 2

## THE HISTORICAL AIR MONITORING DATA BASE

Total suspended particulate matter concentrations have been measured in the Los Angeles area by the South Coast Air Quality Management District (SCAQMD) and by the National Air Surveillance Network (NASN). Data at ten sampling stations have been chosen for use in this study, at the sites indicated in Figure 1.

The South Coast Air Quality Management District network began operation in August 1965 at a few locations, and has expanded over the years. The time frame spanned by the data studied at each monitoring site is indicated in Table 1. Twenty-four hour average particulate data were collected on glass fiber filters by high volume sampling. At times the sampling frequency has ranged from weekly, to twice weekly, to every fifth or sixth day. Total suspended particulate concentrations were determined gravimetrically. Sulfates were measured by either the manual turbidimetric method or automated methylthymol blue method, and nitrates were determined by either the xylenol method or the automated Saltzman method. Seven trace metals (Cu, Cr, Fe, Mn, Ni, Pb, and Zn) were measured by atomic absorption spectrophotometry after direct extraction of a filter section in nitric acid. Sampling and analytical methods are described in detail by Wadley and MacPhee (1976a,b) and by Wadley et al. (1979a,b).

The SCAQMD trace metal sampling program for metals other than lead was terminated in early 1978. As a result, we will analyze data taken through the year 1977, the last full year of trace metal network

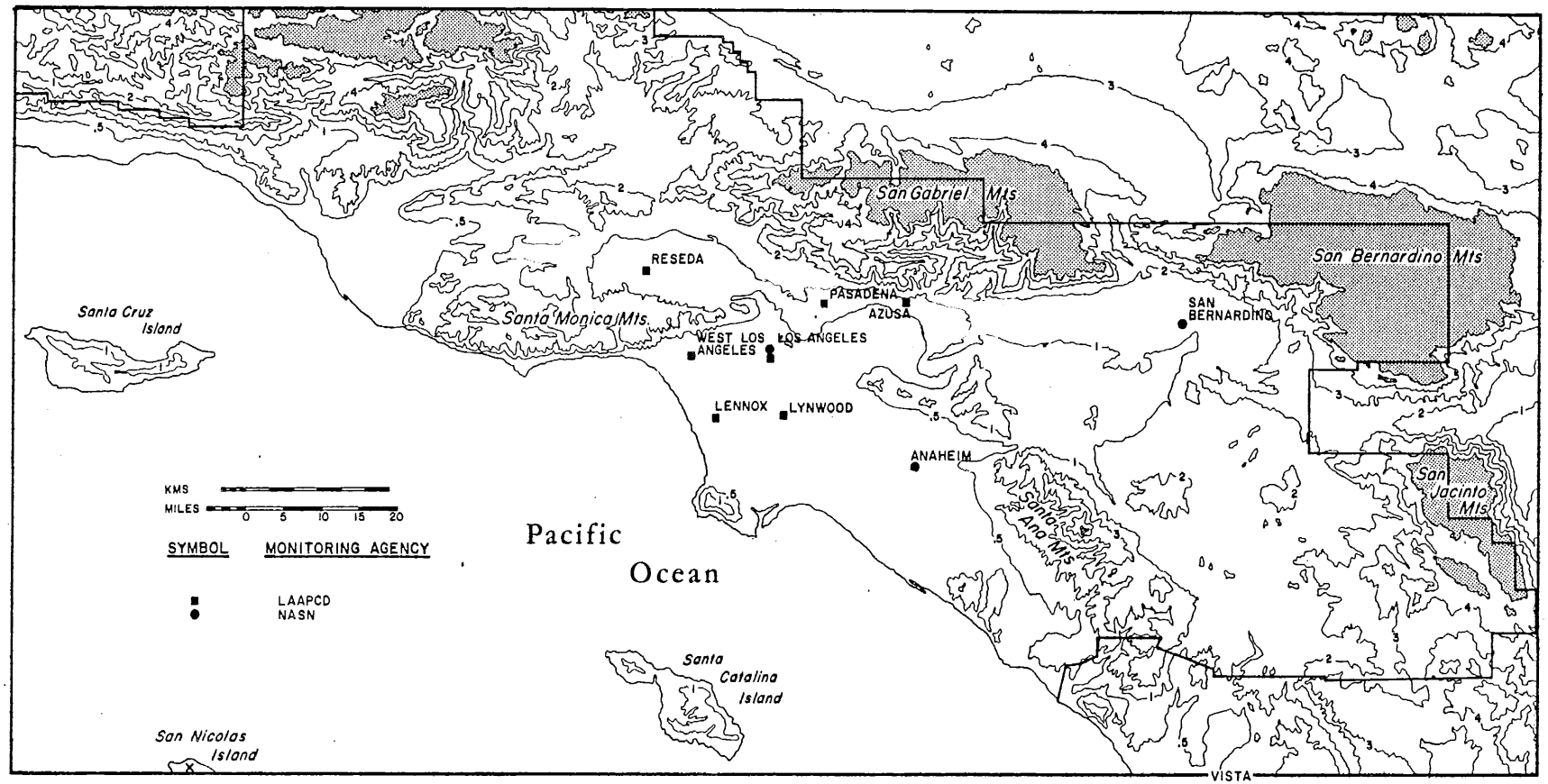



FIGURE 1

Location of Monitoring Sites Within the South Coast Air Basin

TABLE 1

Monitoring Sites and Analysis Periods for Particulate Data Collected Within the South Coast Air Basin

| Monitoring Site | Analysis Period | Monitoring Agency | |
|---|---|---|---|
| | | NASN | SCAQMD |
| Azusa | Jul 1971 - Dec 1977 | | * |
| Downtown Los Angeles | Aug 1965 - Dec 1977 | | * |
| Lennox | Aug 1965 - Dec 1977 | | * |
| Lynwood | Jan 1974 - Dec 1977 | | * |
| Pasadena | Jul 1971 - Dec 1977 | | * |
| Reseda | Sep 1967 - Dec 1977 | | * |
| West Los Angeles | Aug 1965 - Dec 1977 | | * |
| Anaheim | 1969 - 1976 | * | |
| Downtown Los Angeles | 1965 - 1976 | * | |
| San Bernardino | 1969 - 1976 | * | |

Note: The NASN data are quarterly composites

operation. Particulate matter and trace metal concentration data taken at each monitoring site are graphed in time series in Appendix A. A representative set of data taken at the Lennox (SCAQMD) monitoring station are shown in Figures 2 through 11.

In order to supplement the SCAQMD data, three trace metal sampling sites were chosen from among the stations operated by the National Air Surveillance Network. The Downtown Los Angeles NASN high volume sampler was sited at the same location as the Downtown Los Angeles SCAQMD station. Thus Downtown Los Angeles was selected as a common point for comparison of results obtained using data from the two independent sampling systems. The Anaheim and San Bernardino NASN stations were chosen in order to expand the geographic coverage of this study to the south and east of Los Angeles County.

Sample collection and analysis procedures of the National Air Surveillance Newtork are described briefly by the U.S. Environmental Protection Agency (1972) and by Faoro and McMullen (1977). The NASN stations operated by collecting 24-hour particulate samples on glass fiber filters using high volume samplers. From the 1960's through 1975, approximately 27 filter samples were collected annually at each site, while from 1976 onward, samples were collected at 6 day intervals. Quarterly average trace metals concentrations for the elements indicated in Table 2 were measured with an emission spectrograph after extracting a composite formed from portions of all hi-vol filters taken at a single station in each quarter of each year. Trace metals data taken since 1970 are felt to be of higher quality than data from

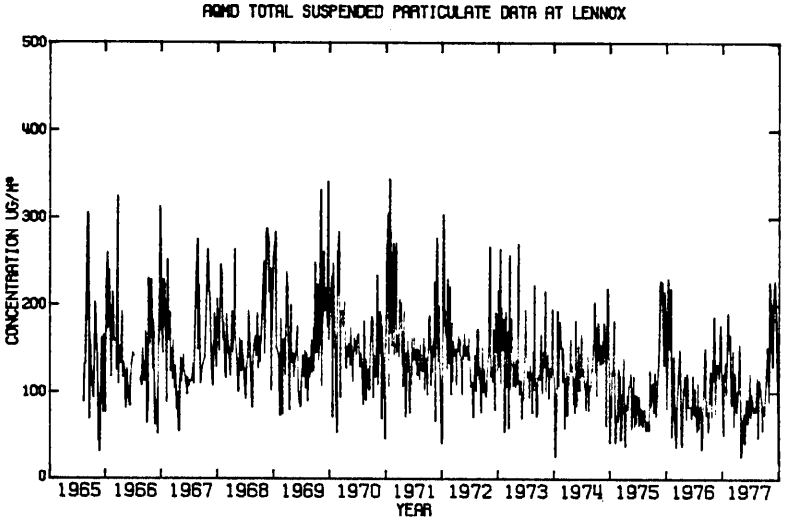



FIGURE 2

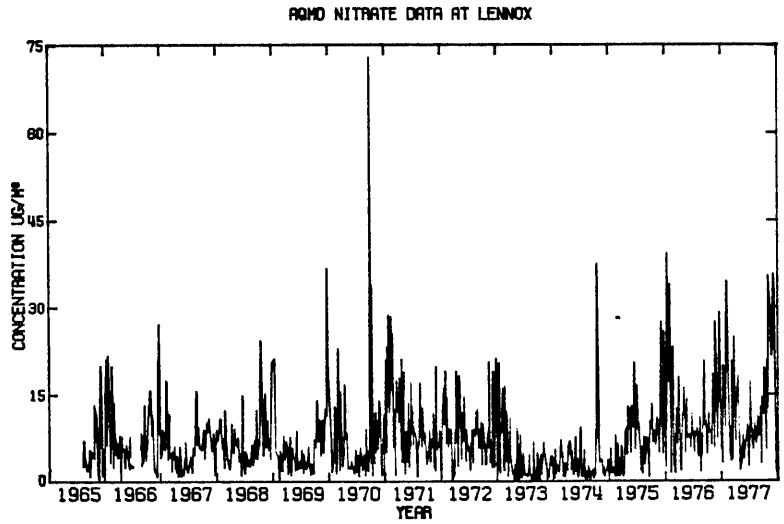



FIGURE 3

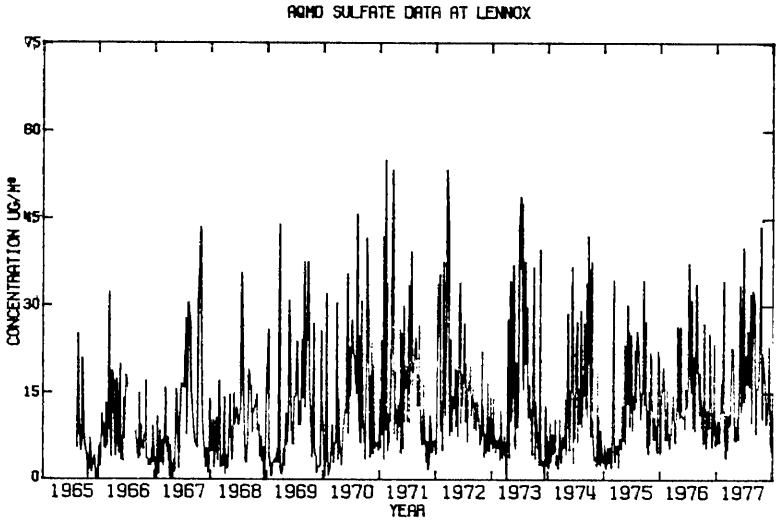



FIGURE 4

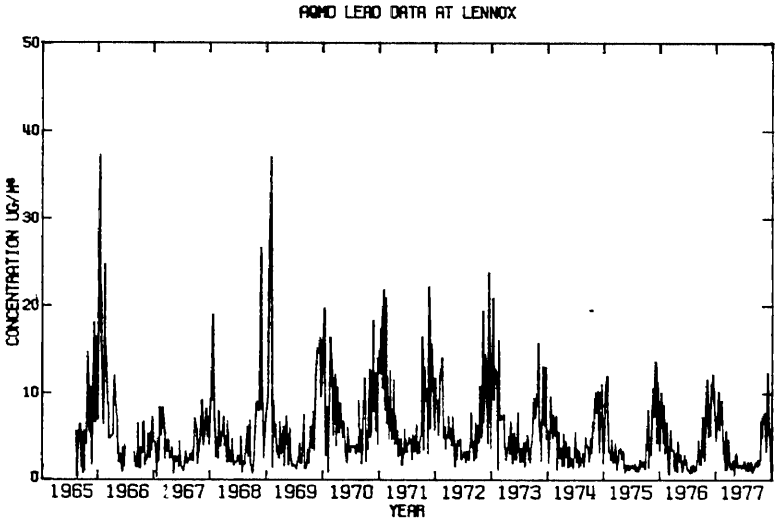
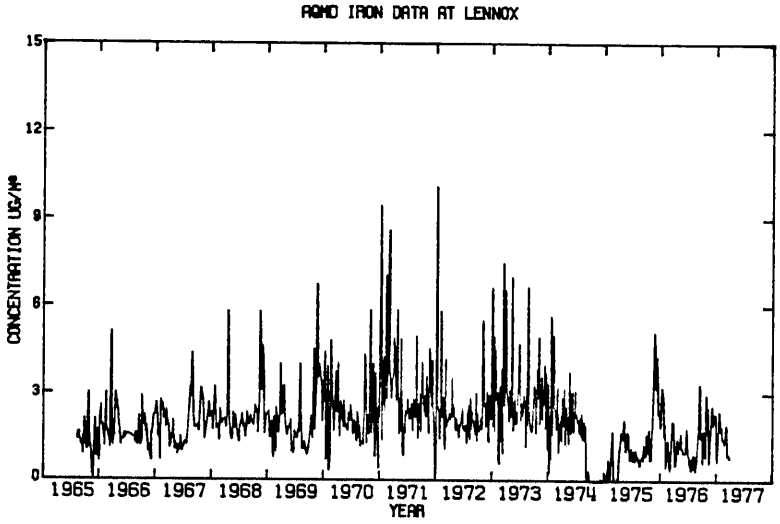



FIGURE 5

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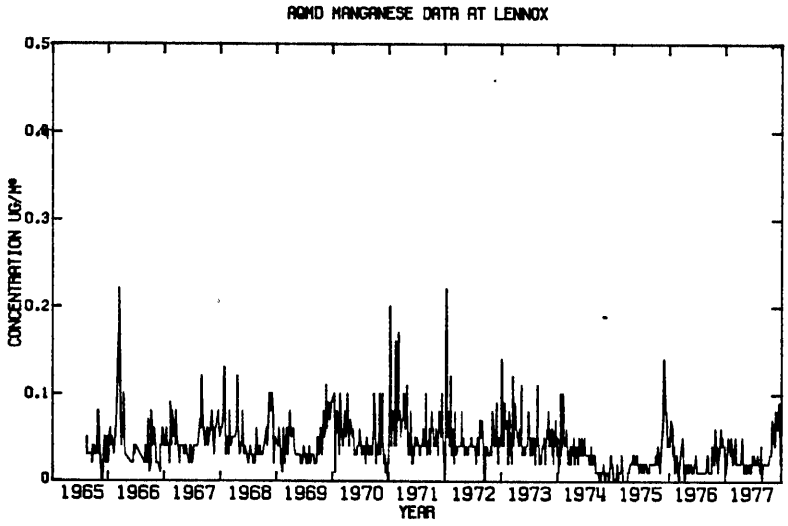


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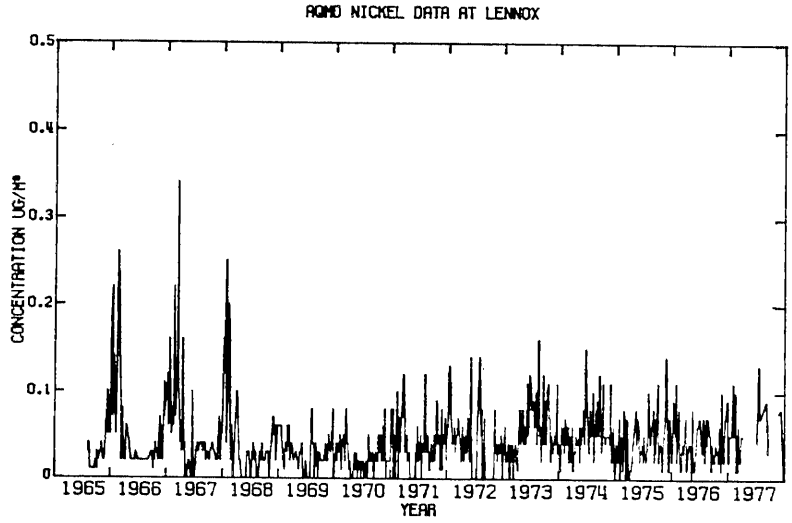
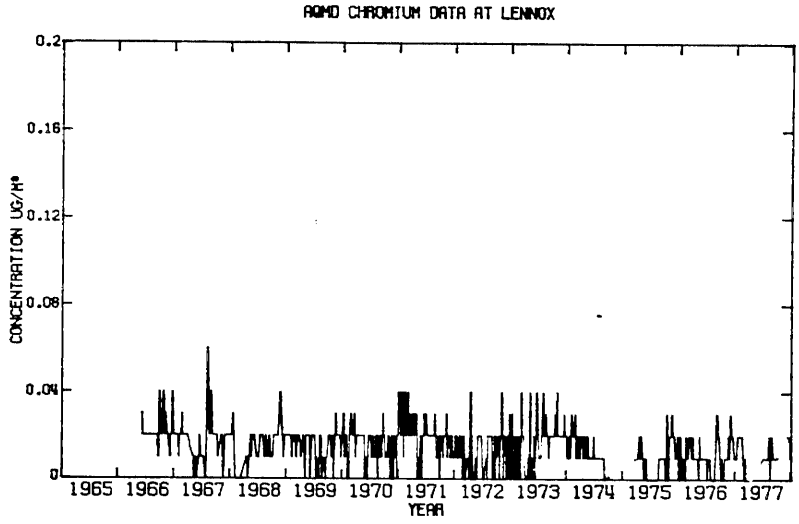



FIGURE 8

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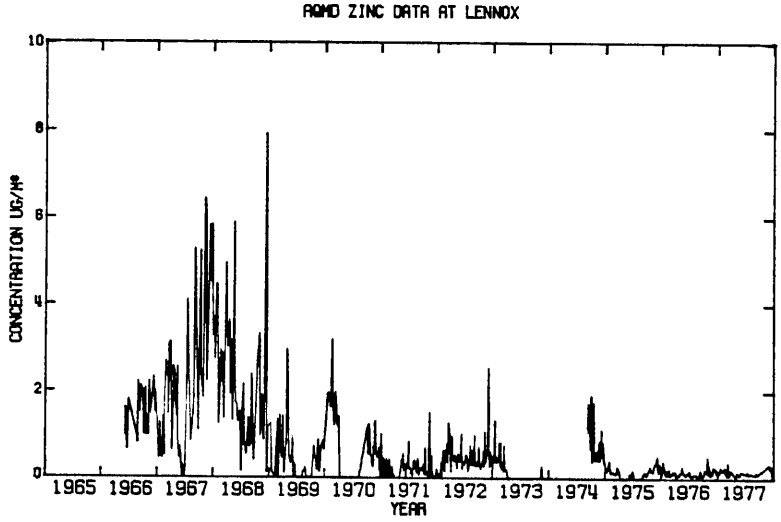



FIGURE 10

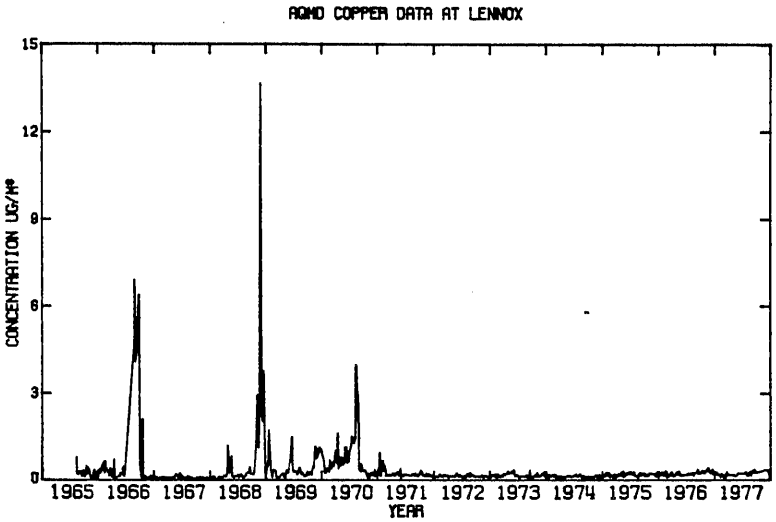



FIGURE 11

TABLE 2

Species Studied at NASN and SCAQMD Monitoring Sites

| Species | Symbol | Monitoring Agency | |
|---|---|---|---|
| | | NASN | SCAQMD |
| Cadmium | Cd | * | |
| Chromium | Cr | * | * |
| Cobalt | Co | * | |
| Copper | Cu | * | * |
| Iron | Fe | * | * |
| Lead | Pb | * | * |
| Manganese | Mn | * | * |
| Nickel | Ni | (a) | * |
| Tin | Sn | * | |
| Titanium | Ti | * | |
| Vanadium | V | * | |
| Zinc | Zn | (a) | * |
| Sulfates | $SO_4^=$ | * | * |
| Nitrates | $NO_3^-$ | * | * |
| Ammonium Ion | $NH_4^+$ | * | |
| TSP | | * | * |

(a) NASN reports (Faoro and McMullen, 1977; U.S. Environmental Protection Agency, 1972) indicate that these metals have been measured in Los Angeles, but they are not included in the data sets furnished to the project by the U.S. Environmental Protection Agency.

earlier years (Faoro and McMullen, 1977). Thus the NASN trace metals data at a monitoring site consist of only four quarterly average concentrations of each element for each year. Although total mass, sulfates, nitrates and ammonium ion data are available for single filter samples, we have averaged all such determinations reported for each quarter year at each NASN site in order to place those data into the same time frame as the trace metals data. NASN quarterly average TSP and trace component concentrations are displayed graphically in Appendix A.

# CHAPTER 3

## TRACE ELEMENT EMISSIONS IN THE SOUTH COAST AIR BASIN

An inventory of aerosol emissions was assembled in the Los Angeles area for each of the trace metals and ionic species measured by the SCAQMD and NASN networks. The objective was to determine which source types dominate the emissions of each chemical substance.

Fuel combustion data combined with information on the level of industrial process and fugitive source activity were used to compute total particulate matter emissions within the geographic region shown in Figure 1. The year 1976 was chosen as the basis for inventory calculations in order to capitalize on the emissions data base of Taback et al. (1979) that was created for that year. The emission inventory results are summarized in Tables 3 through 7. Calculations follow the procedure developed by Cass et al. (1981) and are detailed in Appendix C to this report.

Information on the size distribution and chemical composition of the particulate emissions from major source types are given in Appendix B, based on the work of Miller et al. (1972), Taback et al. (1979), Watson (1979) and others. As seen in the example shown in Table 8, these source profiles identify the fraction of the aerosol mass emitted from each source type that resides in a given particle size range. Then trace element chemical composition is stated as a percentage of the aerosol mass found within each particle size cut.

The source composition profiles were used to subdivide the basin-wide inventory of total particulate emissions into coarse

TABLE 3

Emission Estimates From Mobile Sources

| MOBILE SOURCES | Profile | Estimated Fuel Usage ($10^9$ BTU/day) (a) | Emission Factor | Emissions (kg/day) | Mass Fraction < 10 Micron (%) | Fine Particle Emissions (kg/day) |
|---|---|---|---|---|---|---|
| Highway Vehicles | | | | | | |
| Catalyst Autos & Lt. Trucks | 53 | 368.78 | 2.137 kg/$10^9$BTU | 788. | 100.0 | 788.1 |
| Non-Catalyst Autos & Lt. Trucks | 54 | 1255.16 | 37.814 kg/$10^9$BTU | 47463. | 60.0 | 28477.6 |
| Medium & Heavy Gasoline Vehicles | 54 | 228.17 | 43.596 kg/$10^9$BTU | 9947. | 60.0 | 5968.4 |
| Diesel Vehicles | 52 | 125.52 | 64.200 kg/$10^9$BTU | 8058. | 96.0 | 7736.0 |
| Civil Aviation | | | | | | |
| Jet Aircraft | 55 | 44.56 | U.S. EPA (1976) | 733. | 100.0 | 733.0 |
| Aviation Gasoline | 54 | 1.29 | 9.08 g/LTO cycle | 28. | 60.0 | 16.8 |
| Commercial Shipping | | | | | | |
| Residual Oil-Fired Ships Boilers | 1 | 29.41 | 85.386 kg/$10^9$BTU | 2511. | 87.0 | 2184.7 |
| Diesel Ships | 52 | 17.43 | 49.102 kg/$10^9$BTU | 856. | 96.0 | 821.6 |
| Railroad | | | | | | |
| Diesel Oil | 52 | 19.94 | 81.837 kg/$10^9$BTU | 1632. | 96.0 | 1566.6 |
| Military | | | | | | |
| Gasoline | 54 | 6.03 | 43.596 kg/$10^9$BTU | 263. | 60.0 | 157.7 |
| Diesel Oil | 52 | 17.81 | 78.564 kg/$10^9$BTU | 1399. | 96.0 | 1343.3 |
| Jet Fuel | 55 | 16.71 | U.S. EPA (1976) | 659. | 100.0 | 659.0 |
| Residual Oil (Bunker Fuel) | 1 | 0.27 | 83.386 kg/$10^9$BTU | 23. | 87.0 | 19.6 |
| Miscellaneous | | | | | | |
| Off-Highway Vehicles | 52 | 39.73 | 78.564 kg/$10^9$BTU | 3121. | 96.0 | 2996.5 |
| | | | | | SUB TOTAL | 53468.9 |

TABLE 4

Emission Estimates For Stationary Combustion Sources

| STATIONARY SOURCES | Profile | Estimated Fuel Usage ($10^9$ BTU/day) (a) | Emission Factor | Emissions (kg/day) | Mass Fraction < 10 Micron (%) | Fine Particle Emissions (kg/day) |
|---|---|---|---|---|---|---|
| Fuel Combustion | | | | | | |
| Electric Utilities | | | | | | |
| Natural Gas | 27 | 227.45 | 1.081 kg/$10^9$BTU | 246. | 95.0 | 233.6 |
| Residual Oil (0.50%) | 64 | 993.42 | 21.619 kg/$10^9$BTU | 21477. | 97.0 | 20832.4 |
| Landfill & Digester Gas | 27 | 0.82 | 1.081 kg/$10^9$BTU | 1. | 95.0 | 0.8 |
| Refinery Fuel | | | | | | |
| Natural Gas | 27 | 93.03 | 9.080 kg/$10^9$BTU | 845. | 95.0 | 802.5 |
| Refinery Gas | 27 | 395.95 | 9.080 kg/$10^9$BTU | 3595. | 95.0 | 3415.5 |
| Residual Oil | 1 | 32.97 | 21.619 kg/$10^9$BTU | 713. | 87.0 | 620.1 |
| Non-Refinery Industrial Fuel | | | | | | |
| Natural Gas | 27 | 421.64 | 7.567 kg/$10^9$BTU | 3191. | 95.0 | 3031.0 |
| LPG | 27 | 2.74 | 7.567 kg/$10^9$BTU | 21. | 95.0 | 19.7 |
| Residual Oil | 1 | 53.42 | 21.619 kg/$10^9$BTU | 1155. | 87.0 | 1004.8 |
| Distillate Oil | 2 | 42.74 | 23.520 kg/$10^9$BTU | 1005. | 98.0 | 985.1 |
| Digester Gas (IC Engines) | 50 | 6.30 | 20.430 kg/$10^9$BTU | 129. | 99.0 | 127.4 |
| Coke Oven Gas | 27 | 37.53 | 7.567 kg/$10^9$BTU | 284. | 95.0 | 269.8 |
| Residential/Commercial | | | | | | |
| Natural Gas | 51 | 1181.92 | 8.071 kg/$10^9$BTU | 9539. | 95.0 | 9062.3 |
| LPG | 51 | 18.08 | 8.071 kg/$10^9$BTU | 146. | 100.0 | 145.9 |
| Residual Oil | 1 | 22.19 | 21.619 kg/$10^9$BTU | 480. | 100.0 | 479.7 |
| Distillate Oil | 2 | 22.19 | 21.619 kg/$10^9$BTU | 480. | 98.0 | 470.1 |
| | | | | | SUB TOTAL | 41500.8 |

TABLE 5

Industrial and Fugitive Emissions Based On 1979 AQMP Inventory (July 1981 Version)

| STATIONARY SOURCES | Profile | Emissions (kg/day) | Mass Fraction < 10 Micron (%) | Fine Particle Emissions (kg/day) |
|---|---|---|---|---|
| Industrial Process Point Sources | | | | |
| Petroleum Industry | | | | |
| Refining | 28 | 1943. | 61.0 | 1185.2 |
| Paving and Roofing Materials | 19 | 527. | 98.0 | 516.5 |
| Other (calcining-mineral) | 28 | 454. | 61.0 | 276.9 |
| Organic Solvent Use | | | | |
| Surface Coating | 22 | 772. | 96.0 | 741.1 |
| Printing | 56 | 9. | 99.0 | 8.9 |
| Storage Loss | 56 | 9. | 99.0 | 8.9 |
| Other | 56 | 12. | 99.0 | 11.9 |
| Chemical Plants | 24 | 1952. | 96.0 | 1873.9 |
| Metallurgical Industry | | | | |
| Metals-General | 65 | 1716. | 100.0 | 1716.0 |
| Primary Metals | 65 | 4041. | 100.0 | 4041.0 |
| Secondary metals | | | | |
| Non-Ferrous Metals | 69 | 953. | 95.0 | 905.3 |
| Other | 70 | 799. | 95.0 | 759.0 |
| Metal fabrication | | | | |
| Non-Ferrous Metals | 69 | 1153. | 95.0 | 1095.3 |
| Other | 67 | 409. | 100.0 | 409.0 |
| Mineral Industry | | | | |
| Glass Furnaces | 17 | 708. | 98.0 | 693.8 |
| Rock, Stone, Other | 33 | 10433. | 10.0 | 1043.3 |
| Waste Burning at Point Sources | 5 | 209. | 100.0 | 209.0 |
| Wood and Paper Burning | 5 | 263. | 100.0 | 263.0 |

TABLE 5 (continued)

Industrial and Fugitive Emissions Based On 1979 AQMP Inventory (July 1981 Version)

| STATIONARY SOURCES | Profile | Emissions (kg/day) | Mass Fraction < 10 Micron (%) | Fine Particle Emissions (kg/day) |
|---|---|---|---|---|
| Food and Agriculture | | | | |
| Food and Kindred | 56 | 6637. | 100.0 | 6637.0 |
| Grain Mill and Bakery | 29 | 944. | 29.0 | 273.8 |
| Vegetable Oil | 56 | 236. | 100.0 | 236.0 |
| Other | 29 | 427. | 29.0 | 123.8 |
| Miscellaneous Industrial | | | | |
| Iron and Steel Foundry | 70 | 272. | 100.0 | 272.0 |
| Non-Ferrous Metals | 69 | 182. | 95.0 | 172.9 |
| Other | 67 | 663. | 100.0 | 663.0 |
| Unspecified | 67 | 3514. | 100.0 | 3514.0 |
| | | | SUB TOTAL | 27650.7 |

TABLE 6

Emission Estimates From Other Fugitive Sources

| FUGITIVE SOURCES | Profile | Fine Particle Emissions (kg/day) |
|---|---|---|
| Road and Building Construction | 57 | 176625.0 |
| Agricultural Tilling | 57 | 23633.0 |
| Refuse Disposal Sites | 57 | 746.0 |
| Livestock Feedlots | 59 | 3234.0 |
| Unpaved Road Travel | 57 | 57216.0 |
| Paved Road Travel | 58 | 165400.0 |
| Forest Fires (Seasonal) | 60 | 5790.0 |
| Structural Fires | 35 | 398.4 |
| Fireplaces | 63 | 1244.0 |
| Cigarettes | 39 | 1990.0 |
| Agricultural Burning | 61 | 1244.0 |
| Tire Attrition | 38 | 2409.2 |
| Brake Lining Attrition | 41 | 7712.0 |
| Sea Salt | 62 | 49753.0 |
| | SUB TOTAL | 497394.6 |

TABLE 7

Summary of Particulate Emissions by Element
(Aerodynamic Diameter $d_p$ < 10 Micron)

| Species | Symbol | Fine Particulate Emissions (kg/day) |
|---|---|---|
| Aluminum | Al | 35497.0 |
| Antimony | Sb | 3.4 |
| Arsenic | As | 34.9 |
| Barium | Ba | 193.0 |
| Bismuth | Bi | 0.1 |
| Bromine | Br | 3067.1 |
| Cadmium | Cd | 24.9 |
| Calcium | Ca | 10490.0 |
| Cesium | Cs | 102.3 |
| Chlorine | Cl | 32469.4 |
| Chromium | Cr | 295.5 |
| Cobalt | Co | 118.6 |
| Copper | Cu | 248.2 |
| Iron | Fe | 21149.5 |
| Lanthanum | La | 16.2 |
| Lead | Pb | 8769.9 |
| Magnesium | Mg | 8519.2 |
| Manganese | Mn | 594.2 |
| Molybdenum | Mo | 20.7 |
| Neodymium | Nd | 10.1 |

TABLE 7 (continued)

Summary of Particulate Emissions by Element
(Aerodynamic Diameter $d_p$ < 10 Micron)

| Species | Symbol | Fine Particulate Emissions (kg/day) |
|---|---|---|
| Nickel | Ni | 572.7 |
| Potassium | K | 6791.2 |
| Praeseodymium | Pr | 10.1 |
| Rubidium | Rb | 7.9 |
| Selenium | Se | 148.5 |
| Silicon | Si | 89129.1 |
| Silver | Ag | 3.6 |
| Sodium | Na | 23630.4 |
| Strontium | Sr | 12.7 |
| Tin | Sn | 6.9 |
| Titanium | Ti | 2205.4 |
| Vanadium | V | 160.2 |
| Zinc | Zn | 693.3 |
| Zirconium | Zr | 9.1 |
| Sulfates | $SO_4^{=}$ | 24711.1 |
| Nitrates | $NO_3^-$ | 2197.0 |
| Total Carbon | TC | 89069.8 |
| Elements Listed | | 360983. (58%) |
| Other Emissions | | 259032. (42%) |
| TOTAL EMISSIONS | | 620015. (100%) |

TABLE 8

Example Source Profile

**Industrial Boilers (Number 2 Fuel Oil)**

| Size Range (Micron) | 0-99 | 0-1 | 1-3 | 3-10 | 10-99 | 0-10 |
|---|---|---|---|---|---|---|
| Weight Percent (%) | 100.00 | 96.00 | 0.80 | 0.80 | 2.40 | 97.60 |
| Species | | | | | | |
| Arsenic | 0.55 | 0.55 | 0.05 | 0.05 | 0.05 | 0.542 |
| Cadmium | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| Chromium | 0.55 | 0.55 | 0.05 | 0.05 | 0.05 | 0.542 |
| Lead | 0.55 | 0.55 | 0.55 | 0.55 | 0.55 | 0.55 |
| Nickel | 0.55 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| Selenium | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| Tin | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| Titanium | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| Zinc | 0.55 | 0.55 | 0.55 | 0.55 | 0.55 | 0.55 |
| Sulfates | 25.00 | 25.00 | 25.00 | 25.00 | 25.00 | 25.00 |
| Nitrates | 4.00 | 4.00 | 0.55 | 0.55 | 0.55 | 3.943 |
| Total Carbon | 15.00 | 15.00 | 15.00 | 15.00 | 15.00 | 15.00 |
| (Volatile Carbon) | 14.00 | 14.00 | 14.00 | 14.00 | 14.00 | 14.00 |
| Other | 53.050 | 53.550 | 58.00 | 58.00 | 58.00 | 53.623 |
| Totals | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

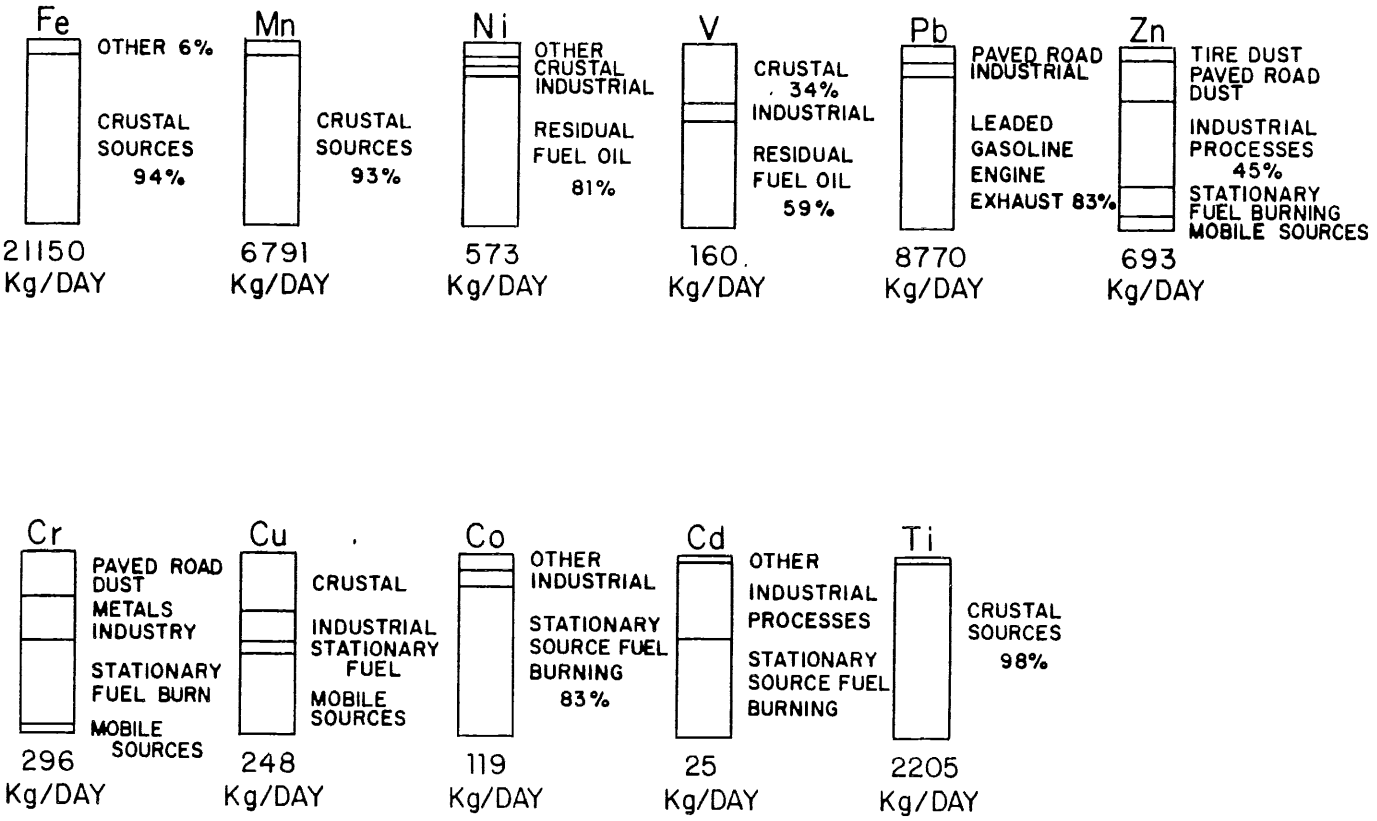
Basis: Taback et al. (1979)

($d_p$ > 10 microns) and fine particle ($d_p \leq$ 10 micron) fractions. Then the fine particle emissions inventory was further subdivided into separate inventories for each of the trace metals of interest. Fine particle emissions are emphasized because particles larger than about 10 microns settle out of the atmosphere rapidly. Thus most coarse material does not reach the regional monitoring sites that will be used for comparison to the emissions data (see the material balance results of Huntzicker et al., 1975). Use of source profiles generated after removing the emissions of large settleable particulate matter provides one means of estimating the effect of atmospheric fractionation( $f_{ij}$ in equation 1).

The fine particle trace metals emissions inventory is detailed in Appendix C and summarized in Figure 12. Emissions of fine particle iron, manganese and titanium are dominated by soil dust-like sources, with greater than 90% of these emissions derived from the earth's crust. In a similar fashion, 83% of the airborne lead is emitted from engines burning leaded gasoline. Another 9% of the fine lead emissions come indirectly from vehicle exhaust in the form of resuspended road dust. Over 80% of fine nickel emissions are estimated to arise from residual fuel oil combustion. Nickel appears to be a better tracer for fuel oil combustion than vanadium in Los Angeles. As seen in Figure 12, vanadium emissions are split between fuel oil combustion and soil-like crustal sources. These source assignments made on the basis of emissions data are consistent with the inferences drawn from air quality measurements made in Pasadena by Hammerele and Pierson (1975). They attribute iron, manganese and titanium to soil dust, lead to

FIGURE 12

Fine Particle Trace Metals Emissions by Element (1976)



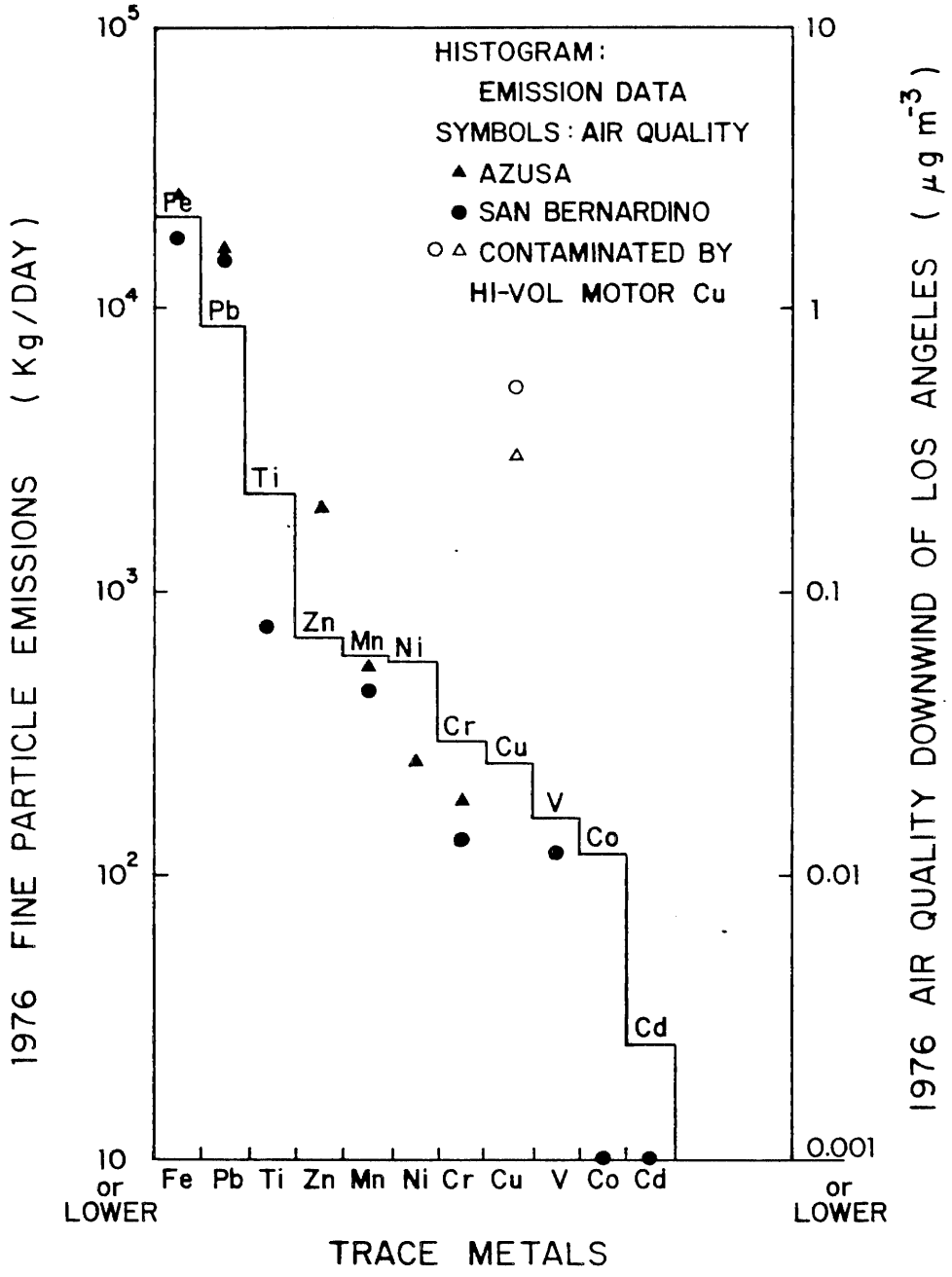
leaded gasoline use, and note that vanadium is correlated with nickel but displays a size distribution half way between the Pb, Br, Ni and Zn group (that is all in very small particles) and the Fe, Mn, Ti group (soil-like materials that appear in larger particle sizes).

The remaining metals under study at our monitoring sites include Zn, Cd, Cr, Co and Cu. Most of these metals arise from small contributions from a large number of diverse sources that have been grouped together in Figure 12. Zinc is particularly interesting. It has been attributed mostly to tire dust or to municipal incineration in past receptor modeling studies (see for example Friedlander, 1973; Kowalczyk et al. 1978). The emission inventory Tables in Appendix C shows that zinc is emitted from 40 source classes. It is going to be almost impossible to account for zinc sources correctly in a chemical element balance for Los Angeles unless a large number of source signatures (and elements) are used in the data reduction process. Chromium, copper and cadmium likewise are emitted from a diversity of sources. The cobalt emissions inventory is suspect; much of the cobalt emissions were estimated from source tests on combustion equipment burning natural gas or process gas that may have been contaminated by a previous history of oil burning.

Emission inventory results for trace metals are compared to ambient air monitoring data in Figure 13. Since the emissions data are integrated over the whole Los Angeles urban area, the air monitoring sites shown for comparison are those farthest downwind of the city within the Los Angeles plume. The relative abundance of trace metals

FIGURE 13

Trace Metals in the South Coast Air Basin:
Comparison of Emissions and Air Quality Data



in both the emissions and air quality data sets are well matched, except for copper and cobalt. The ambient copper measurements are known to be contaminated by copper worn from high volume sampler motors (Radke et al., 1977). The cobalt emission estimates are suspect, as mentioned previously.

# CHAPTER 4

## KEY EMISSIONS SOURCES

The particulate composition data available at routine monitoring sites are not detailed enough to carefully account for all of the major aerosol sources affecting that monitoring site. Data on the best soil dust tracers, silicon and aluminum, are unavailable. In a similar fashion, we lack data on sodium as a sea salt tracer and calcium as a key component of cement and gypsum dust. But after reviewing the list of chemical data that we do have, several likely candidate tracer elements can be associated with major source types. In particular from Figure 12 we note that fuel oil fly ash dominates the nickel emissions in the Los Angeles area, auto exhaust controls the suspended lead, and crustal material (soil or road dust) is the largest source of iron and manganese. In addition, the sulfate and nitrate data available account for much of the secondary aerosol present. Chemical composition estimates for each of these key source types are given in Table 9 and will form the basis for a variety of receptor modeling calculations. Because of the importance of these particular profiles, each will be discussed briefly.

Measured sulfate species initially will be assumed to have an average molecular weight like that of ammonium sulfate. For use in later calculations, a transformed variable will be defined:

$$\text{SULFATES}_j = 1.38 \quad SO_{4_j}^{=} \qquad (2)$$

TABLE 9

The Chemical Composition of Selected Sources of Atmospheric Fine Particulate Matter

| Chemical Component (a) | Percentages (%) Soil Dust (b) | Road Dust (c) | Fuel Oil Fly Ash (d) | Highway Aerosol (e) | Ammonium Sulfate | Ammonium Nitrate |
|---|---|---|---|---|---|---|
| $SO_4^=$ | | 0.62 | 31.9 | 1.40 | 72.7 | |
| $NO_3^-$ | | 0.42 | 4.50 | 0.1 | | |
| Fe | 3.2 | 6.92 | 1.13 | 0.333 | | 77.5 |
| Mn | 0.11 | 0.137 | 0.052 | 0.0039 | | |
| Ni | 0.004 | 0.012 | 2.12 | 0.0002 | | |
| Pb | 0.02 | 0.47 | 0.064 | 12.8 | | |
| Cr | | 0.04 | 0.128 | | | |
| Cu | 0.008 | 0.032 | 0.042 | 0.10 | | |
| Zn | 0.005[f] | 0.11 | 0.101 | 0.151 | | |
| V | 0.006 | 0.023 | 0.339 | 0.0014 | | |
| Cd | | | 0.022 | | | |
| Co | 0.002 | | 0.047 | | | |
| Sn | | | | | | |
| Ti | 0.4 | 0.67 | 0.008 | | | |

(a) Chemical components listed are those under study in the SCAQMD and NASN ambient air quality data base. For complete source composition profiles, see Appendix B.

(b) Resuspended soil dust samples taken in the Los Angeles area (Friedlander, 1973).

(c) Road dust fine particle samples taken in Portland, Oregon (Watson, 1979)

(d) Direct average of elemental percentages obtained by Taback et al. (1979) in South Coast Air Basin utility boiler tests 11, 12, 13, 21, 22, 24, 32, 33 as reported in "Total" columns of Tables 4-26 to 4-33.

(e) Composite of gasoline and diesel powered highway vehicle exhaust, plus tire and brake dust. (See Table 13)

(f) Given as < 0.01 %

where

$SULFATES_j$ stands for sulfate salt concentration in the atmosphere on day j in micrograms per cubic meter.

$SO_{4_j}^{=}$ is the sulfate ion concentration as measured by high volume sampling on day j.

The factor 1.38 is a stoichiometric coefficient relating the molecular weight of ammonium sulfate to that of the $SO_4^{=}$ ion. The factor 1.38 will vary from monitoring site to monitoring site because other sulfate species like ammonium bisulfate and sulfuric acid have lower molecular weights. If sulfuric acid were present, a coefficient of 1.02 would be appropriate.

In a similar fashion, the amount of each day's particulate matter that was associated with nitrates will be estimated as if those compounds were ammonium nitrate:

$$NITRATES_j = 1.29 \; NO_{3_j}^{-} \qquad (3)$$

where

$NITRATES_j$ is the mass of nitrate compounds in the aerosol on day j.

$NO_{3_j}^{-}$ is the measured nitrate ion mass concentration on day j.

From Table 10 we note that iron and manganese are very highly correlated ($r = 0.89$), indicating that they probably come from a common source. These elements are as close to a soil dust tracer as we will find in the SCAQMD and NASN air monitoring data bases. The ratio of the average values of iron to manganese from Table 10 is 47:1 while the ratio from Table 11 is 53:1. These values are somewhat higher than the

TABLE 10

SCAQMD Particulate Air Quality Data at Downtown Los Angeles
[742 Samples Considered]

Aug. 1965 - Dec. 1977

| | TSP | $SO_4^=$ | $NO_3^-$ | Pb | Fe | Mn | Ni |
|---|---|---|---|---|---|---|---|
| MEAN | 140.80 | 12.80 | 10.88 | 3.90 | 2.18 | 0.046 | 0.033 |
| STANDARD DEVIATION | 59.60 | 10.71 | 8.48 | 2.70 | 1.31 | 0.028 | 0.031 |

CORRELATION MATRIX

| | TSP | $SO_4^=$ | $NO_3^-$ | Pb | Fe | Mn | Ni |
|---|---|---|---|---|---|---|---|
| TSP | 1.00 | 0.39 | 0.45 | 0.60 | 0.65 | 0.68 | 0.34 |
| $SO_4^=$ | | 1.00 | 0.09 | 0.01 | 0.03 | 0.08 | 0.10 |
| $NO_3^-$ | | | 1.00 | 0.35 | 0.28 | 0.30 | 0.16 |
| Pb | | | | 1.00 | 0.46 | 0.44 | 0.40 |
| Fe | | | | | 1.00 | 0.89* | 0.24 |
| Mn | | | | | | 1.00 | 0.27 |
| Ni | | | | | | | 1.00 |

All pollutant concentrations are in $\mu g\ m^{-3}$.

*737 Sample Pairs

TABLE 11

NASN Particulate Air Quality Data at Downtown Los Angeles
[38 Quarters Considered]

1965 - 1976

| | TSP | $SO_4^=$ | $NO_3^-$ | $NH_4^+$ | Pb | Fe | Mn | V | Ti | Cr | Cu |
|---|---|---|---|---|---|---|---|---|---|---|---|
| MEAN | 119.42 | 11.37 | 10.40 | 1.06 | 3.52 | 1.75 | 0.033 | 0.011 | 0.059 | 0.013 | 0.089 |
| STANDARD DEVIATION | 30.27 | 4.53 | 4.33 | 1.17 | 1.86 | 0.56 | 0.012 | 0.014 | 0.032 | 0.006 | 0.045 |

CORRELATION MATRIX

| | TSP | $SO_4^=$ | $NO_3^-$ | $NH_4^+$ | Pb | Fe | Mn | V | Ti | Cr | Cu |
|---|---|---|---|---|---|---|---|---|---|---|---|
| TSP | 1.00 | 0.37 | 0.34 | 0.16 | 0.36 | 0.63 | 0.54 | 0.002 | 0.47 | 0.27 | -0.12 |
| $SO_4$ | | 1.00 | 0.22 | 0.47 | -0.19 | -0.15 | -0.12 | -0.003 | 0.12 | -0.13 | -0.02 |
| $NO_3$ | | | 1.00 | 0.11 | -0.15 | 0.10 | 0.03 | -0.33 | 0.50 | -0.05 | -0.29 |
| $NH_4$ | | | | 1.00 | -0.02 | -0.24 | -0.07 | 0.28 | -0.02 | 0.01 | 0.14 |
| Pb | | | | | 1.00 | 0.64 | 0.60 | 0.42 | -0.03 | 0.68 | 0.38 |
| Fe | | | | | | 1.00 | 0.80 | 0.04 | 0.44 | 0.61 | 0.10 |
| Mn | | | | | | | 1.00 | 0.12 | 0.33 | 0.54 | 0.30 |
| V | | | | | | | | 1.00 | -0.12 | 0.35 | 0.49 |
| Ti | | | | | | | | | 1.00 | 0.07 | -0.16 |
| Cr | | | | | | | | | | 1.00 | 0.44 |
| Cu | | | | | | | | | | | 1.00 |

All pollutant concentrations are in $\mu g\ m^{-3}$.

29:1 ratio of iron to manganese indicated by Friedlander's (1973) soil chemistry data of Table 9, but they closely match the 50:1 ratio present in Watson's (1979) fine particle road dust samples. The soil dust and road dust samples contain almost exactly the same mass fraction of manganese. Therefore we will use manganese as our tracer element for crustal material. From Table 9, we expect that manganese will constitute 0.11% of the soil dust mass. Thus,

$$CRUSTAL_j = 909.1 \; Mn_j \qquad (4)$$

where

$CRUSTAL_j$ is the concentration of soil dust-like crustal material measured on day j.

$Mn_j$ is the manganese concentration measured on day j.

Nickel is a likely tracer for fuel oil fly ash. From Table 9 one would estimate that nickel constitutes about 2.12% of the particulate emissions from low sulfur oil combustion. Thus

$$OIL\ ASH_j = 47.2 \cdot Ni_j \qquad (5)$$

where

$OIL\ ASH_j$ is the fuel oil fly ash contribution to the particulate matter on day j.

$Ni_j$ is the measured ambient nickel concentration on day j.

Vanadium has been used as a fuel oil tracer in the northeastern United States (Kniep et al., 1972; Kleinman et al., 1980), and also has been proposed as a fuel oil tracer in Los Angeles (White and Roberts, 1977; Hidy et al., 1974). Our emission inventory suggests that

vanadium emissions may be divided between fuel oil use and crustal sources at present in Los Angeles. But in order to further test the usefulness of vanadium as a local fuel oil fly ash tracer, an alternate formulation of the OIL ASH variable will be defined

$$\text{OIL ASH}_j = 255\ V_j \qquad (6)$$

where

$V_j$ is the measured ambient vanadium concentration during sampling period j.

It must be remembered that fuel oil is not a uniform product, and that the trace metals in fuel oil vary greatly from one crude oil stock to another. For example, the vanadium to nickel ratio in fuel oil ash from Table 9 is 0.16:1. However, earlier source measurements made in the Los Angeles basin show a vanadium to nickel ratio of nearly 3.5:1 (Friedlander, 1973) with nickel also present as 2% of the fly ash mass. We would suggest that an inquiry be made to determine if local utility companies have made periodic measurements of the chemical composition of the particulate emissions from their power plants. If those data exist, they should be combined with the data of Taback et al. (1979) and used to improve the stoichiometric coefficient estimates in equations (5) and (6).

Studies by Huntzicker et al. (1975) show that virtually all of the lead present in the Los Angeles atmosphere originated in the combustion of leaded gasoline. The emissions inventory results of Figure 12 confirm that finding. As noted by Kowalczyk et al. (1978), these aerosol lead emissions act as a tracer for all highway-derived emissions,

including both gasoline powered and diesel powered vehicles. Depending on the mix of vehicles present, the lead content of the fuel and the ratio of leaded to unleaded gasoline use, the mass fraction lead in the total vehicle-derived aerosol can range from 4% to 40% (Pierson and Brachaczek, 1976; Kowalczyk et al., 1978; and Watson, 1979). Therefore, for use in the present study a HIGHWAY vehicle source profile will be constructed that is specific to a composite of Los Angeles area traffic emissions. The procedure for developing such a highway signature from emissions inventory data is given by Cass et al. (1981).

Use of lead as a tracer for auto exhaust is complicated by the fact that much of the automotive lead is emitted in large particles (greater than 9 microns aerodynamic particle diameter) that should undergo rapid gravitational settling. Large settleable particles may never reach our monitoring sites. Thus an emission profile is sought that represents the chemical composition of only the fine particle fraction of leaded fuel vehicle exhaust.

Fine aerosol emissions from autos burning leaded gasoline were treated as consisting largely of carbon particles plus lead salts. The lead content of Southern California gasolines is given in Table 12. Assuming a lead content of 2g/gal in leaded gasoline, representative of the year 1976, fine particle lead salt and carbon particle emissions from automobiles burning leaded fuel were computed as shown in footnote (a) to Table 13. The resulting estimate that lead should consitute 21.1% of the mass of fine particulate matter emitted from cars burning leaded gasoline is in excellent agreement with the literature survey discussed by Watson (1979).

TABLE 12

Scale Factors Relating Lead Concentrations Sampled to Aerosol Present from Automobiles Burning Leaded Fuel and from all Highway Traffic

| Time Period | Lead Content of Gasoline (g/gallon) | | |
|---|---|---|---|
| | Regular | Premium | Average |
| Summer 1965 | 2.14 | 3.04 | 2.59 |
| Winter 1965-66 | 1.87 | 3.23 | 2.55 |
| Summer 1966 | 2.28 | 3.07 | 2.68 |
| Winter 1966-67 | 2.14 | 2.87 | 2.51 |
| Summer 1967 | 2.52 | 3.05 | 2.79 |
| Winter 1967-68 | 2.10 | 2.72 | 2.41 |
| Summer 1968 | 2.19 | 3.02 | 2.61 |
| Winter 1968-69 | 1.78 | 2.52 | 2.15 |
| Summer 1969 | 2.03 | 2.92 | 2.48 |
| Winter 1969-70 | 2.19 | 2.82 | 2.51 |
| Summer 1970 | 1.83 | 2.73 | 2.28 |
| Winter 1970-71 | 1.53 | 2.89 | 2.21 |
| Summer 1971 | 1.66 | 2.75 | 2.21 |
| Winter 1971-72 | 1.50 | 2.75 | 2.13 |
| Summer 1972 | 1.25 | 2.70 | 1.98 |
| Winter 1972-73 | 1.24 | 2.64 | 1.94 |
| Summer 1973 | 1.40 | 2.65 | 2.03 |
| Winter 1973-74 | 1.16 | 2.39 | 1.78 |
| Summer 1974 | 1.40 | 2.60 | 2.00 |
| Winter 1974-75 | 1.42 | 2.50 | 1.96 |
| Summer 1975 | 1.17 | 2.40 | 1.79 |
| Winter 1975-76 | 1.42 | 2.40 | 1.91 |
| Summer 1976 | 1.44 | 2.67 | 2.06 |
| Winter 1976-77 | 1.35 | 2.32 | 1.84 |
| Summer 1977 | 1.22 | 2.53 | 1.88 |
| Winter 1977-78 | 1.10 | 2.03 | 1.57 |
| Summer 1978 | 1.10 | 1.87 | 1.49 |
| Winter 1978-79 | 0.90 | 1.82 | 1.36 |

Reference:

Lead content of gasoline from U.S. Bureau of Mines (1966) et seq.

TABLE 13

Source Profiles for Fine Aerosol Emissions
from Highway Vehicles

| | Gasoline Autos and Trucks (Leaded Fuel) (a) | Automobile (Unleaded) (b) | Diesel Engine (c) | Tire Tread (d) | Brake Lining (e) | Highway Composite (f) |
|---|---|---|---|---|---|---|
| 1976 Mass Emissions ($d_p$ < 10 micron) | | | | | | |
| (Tons/day) | 34.75 (60.7%) | 0.79 (1.39%) | 7.74 (13.6%) | 6.04 (10.6%) | 7.71 (13.6%) | 56.71 |
| Chemical Composition(%) | | | | | | |
| Aluminum | 0.043 | 0.12 | 0.34 | | | 0.074 |
| Bromine | 8.2 | | 0.031 | | | 4.98 |
| Calcium | | 0.17 | 0.84 | | 5.5 | 0.86 |
| Chlorine | 5.4 | | 1.69 | | | 3.51 |
| Copper | 0.004 | 0.024 | 0.73 | | | 0.10 |
| Iron | 0.25 | 0.11 | 1.32 | | | 0.333 |
| Lead | 21.1 | | 0.095 | | | 12.8 |
| Magnesium | | | | | 8.25 | 1.12 |
| Manganese | | 0.015 | 0.027 | | | 0.0039 |
| Nickel | | 0.015 | | | | 0.0002 |
| Potassium | | 0.044 | | | | 0.001 |
| Silicon | 0.075 | 0.51 | 0.17 | | 15.4 | 2.17 |
| Sodium | | | 0.37 | | | 0.05 |
| Vanadium | | | 0.01 | | | 0.00136 |
| Zinc | 0.021 | 0.08 | 0.23 | 1.0 | | 0.151 |
| Sulfates | 0.213 | 50.0 | 4.2 | | | 1.40 |
| Nitrates | | | 0.72 | | | 0.1 |
| Carbon | 54.5 | 39.0 | 70.0 | 87.0 | 28.3 | 56.2 |

Footnotes for Table 13

(a) The procedure used to estimate the composite profile for the fine particle emissions from leaded fuel combustion is as follows:

1. 2g Pb/gal in gasoline in mid-1970's in Los Angeles; at an average mileage of 13.6 miles/gal the equivalent Pb emission rate is 0.147 g/mile.

2. From Huntzicker et al. (1975), 70.5% of Pb is emitted as aerosol, and only 43% of that material is in particle sizes less than 9 microns in aerodynamic diameter: thus 44.7 mg/mile is emitted as fine lead aerosol.

3. Fine particle lead is emitted as lead salts, assumed to be $2PbBrCl.NH_4Cl$ (Habibi, 1973), giving 75.4 mg/mile of fine lead salts.

4. The carbon emitted from older cars (30,000-100,000 accumulated miles) is about 115 mg/mile from Ter Haar in Habibi (1973). Carbon aerosols are assumed to be concentrated in the fine particle fraction. Of that carbon about 9 mg/mile is non-volatile "elemental carbon" (Cass et al.; 1981). The remaining carbon is assumed to be present as a typical organic compound (organics = 1.2 x organic carbon). Total organics mass is then 127 mg/mile. The total fine aerosol mass emission rate is approximately 75.4 + 127 + 9 = 211.4 mg/mile.

5. Major fine aerosol components are: lead 44.7 mg/mile (21%), Br 17.2 mg/mile (8.2%), Cl 11.5 mg/mile (5.4%), and Carbon 115 mg/mile (54.5%).

6. Other minor aerosol components shown in the profile were taken from Watson's (1979, page 96), leaded automobile exhaust profile fine particle fraction, except for sulfates that were estimated at 0.45 mg/mile for 0.05% S in the gasoline. The sulfate estimate is based on a scale-up of estimates by Pierson (1977), who suggested 0.27 mg/mile sulfates from pre-catalyst cars using fuel with 0.03% S.

(b) This is a composite profile estimated as follows: sulfate fraction from Laresgoti and Springer (1977); carbon fraction from Mulhbaier and Williams (1981); other trace species from Watson (1979) unleaded auto fine particle profile (ignoring lead and bromine that were probably due to use of leaded fuel at some point).

(c) Watson (1979), page 101, diesel truck fine particle profile modified by insertion of carbon estimates from Cass et al.(1981).

Footnotes for Table 13 (Continued)

(d) Carbon content computed from tire tread formula given by Morton (1973); zinc content given from test results of Pierson and Brachaczek (1974).

(e) Lynch (1968), automobile brake linings are 55% asbestos, 28% resins and polymers, 9% oxides and pigments, metals 3%, carbon and graphite 5%. Resins and polymers were taken to be 1.2 x organic carbon present. Graphite was equated with the non-volatile carbon. The composition of asbestos was assumed to be Tremolite $[Ca_2Mg_5(Si_4O_{11})_2(OH)_2]_n$, from Dillard and Goldberg (1971).

(f) Composite of profiles given in columns (a)-(e), weighted in proportion to 1976 South Coast Air Basin emissions in each category.

Emission profiles also were estimated for the fine aerosol fraction of the exhaust from gasoline engines burning unleaded fuel, diesel engines, tire dust, and brake lining material. These profiles are shown in Table 13 along with a brief description of the technique used for profile estimation. When weighted by the 1976 South Coast Air Basin mass emissions in each category (See Tables 3 and 6; emissions from use of leaded gasoline in cars and trucks are combined), a composite profile is obtained for highway traffic. This composite forms the basis of the HIGHWAY profile appearing in Table 9. The HIGHWAY profile estimated for Los Angeles from emissions data can be compared to the motor vehicle traffic aerosol composition obtained from measurements inside a highway tunnel by Ondov (1974) as cited by Kowalczyk et al. (1978). The comparison is quite close as shown in Table 14.

For the year 1976, and for most earlier years, the ratio of fine lead mass to total fine highway aerosol mass can be estimated from Table 13. As before, a scale factor will be established for use in subsequent calculations.

$$HIGHWAY_j = 7.81\ Pb_j \qquad (7)$$

where

$HIGHWAY_j$ is the fine suspendible aerosol contributed by all highway vehicle sources on day j.

$Pb_j$ is the lead measured on day j.

In more recent years, an appropriate scale factor relating ambient aerosol lead to total highway aerosol mass must be recomputed on an

TABLE 14

Comparison of HIGHWAY Profile to Highway Tunnel Data
(Elemental Abundance Shown Relative to Lead Content)

| Element (a) | Motor Vehicle Profile from Tunnel Measurements (b) | Los Angeles HIGHWAY Profile from the (1976) Emission Inventory (c) |
|---|---|---|
| Lead | = 1.00 | = 1.00 |
| Barium | 0.013 | Unknown |
| Bromine | 0.38 | 0.39 |
| Calcium | 0.05 | 0.067 |
| Chlorine | 0.10 | 0.27 |
| Iron | 0.05 | 0.03 |
| Zinc | 0.015 | 0.012 |

(a) Comparison possible only for elements given by Kowalczyk et al. (1978).

(b) From Ondov (1974) as cited by Kowalczyk et al. (1978).

(c) From Table 13.

annual basis. The problem becomes complicated by the fact the lead content of gasoline is declining and that autos burning leaded fuel are being progressively phased out of the vehicle fleet, causing the highway aerosol mass to lead ratio to rise over time. It is estimated that fine aerosol emissions from highway vehicles in Los Angeles in 1980 totaled about 15.5 times the fine lead emissions rate, as detailed in Table 15.

The Lennox air monitoring site must be treated as a special case. The Lennox station is located so close to the San Diego Freeway that some large particle lead is likely to remain airborne for the short distance needed to reach that sampler. Air quality modeling studies by Cass (1975) show that suspendible lead particles below 9 microns aerodynamic diameter would account for only 3.0 of the 4.18 microgram per cubic meter of lead measured at Lennox in 1969. The implication is that about 30% of the lead emitted in larger particle sizes must be reaching the Lennox sampling station. Assume that virtually all of the automotive carbon is in small suspendible particles (see Habibi, 1973), that bromine and chlorine increase in proportion to the increase in airborne lead, and that only 70% of the large lead particles that will deposit quickly have deposited before reaching the Lennox station. Repeating the calculation procedure given in footnote (a) of Table 13, the effective emission rate of <u>suspended</u> aerosol seen at Lennox from an older automobile burning gasoline containing 2 g lead/gal would be 241.4 mg/mile, including: lead 62.6 mg/mile (25.9%); Br 24.1 mg/mile (10.0%); Cl 16.1 mg/mile (6.7%); and carbon 115 mg/mile (47.6%). The mass emission rate of minor trace components will be assumed to remain

TABLE 15

Computation of Highway Aerosol
to Lead Mass Ratio for Suspendible Particles
($d_p$ < 10 micron aerodynamic diameter)

| | Early 1980 Fine Particle Mass Emissions (Kg/Day)(a)(b)(c) | |
|---|---|---|
| A. SOURCE TYPE | | |
| Catalyst-equipped autos & light trucks | 2059 | |
| Non-catalyst autos & light trucks | 11359 | |
| Medium and heavy gasoline trucks | 5760 | |
| Diesel highway vehicles | 9082 | |
| Tire dust | 6023 | |
| Brake dust | 7712 | |
| Total Mass | 41995 | Kg/day |
| B. FINE LEAD EMISSIONS | 2715 | Kg/day |
| C. $\frac{\text{Highway Fine Particle Emissions}}{\text{Fine Lead Emissions}}$ = | 15.5 | |

(a) From Cass et al. (1981).

(b) Within the 1974 boundaries of the South Coast Air Basin.

(c) Emissions in sizes less than 10 micron aerodynamic diameter.

unchanged, but their fractional representation in the leaded auto profile for Lennox will be diluted by the increased presence of lead salts.

A revised HIGHWAY aerosol profile was recomputed for near freeway conditions like those at Lennox, based on a weighted average of the Lennox leaded auto exhaust profile plus the profiles for unleaded gasoline use, diesel vehicles, tire dust and brake dust. The Lennox HIGHWAY profile is shown in Table 16. At a lead content of 17.7%, the scale factor relating aerosol mass from highway vehicles to lead observed at Lennox becomes:

$$HIGHWAY_j \text{ (Lennox)} = 5.65\ Pb_j \qquad (8)$$

TABLE 16

Source Profiles for Suspended Particulate Emissions from Highway Vehicles at the Lennox Near-Freeway Monitoring Site

| Chemical Component (a) | Percentages (%) Autos and Trucks Burning Leaded Gasoline (Near-Freeway Case) (b) | Lead Enriched Highway Aerosol (c) |
|---|---|---|
| $SO_4^=$ | 0.188 | 1.285 |
| $NO_3^-$ | | 0.069 |
| Fe | 0.219 | 0.307 |
| Mn | | 0.0036 |
| Ni | | 0.0002 |
| Pb | 25.9 | 17.7 |
| Cr | | |
| Cu | 0.0035 | 0.092 |
| Zn | 0.018 | 0.139 |
| V | | 0.0013 |
| Cd | | |
| Co | | |
| Sn | | |
| Ti | | |

(a) Chemical components listed are those under study in the SCAQMD and NASN ambient air quality data base. For complete source composition profiles, see Appendix B.

(b) Lead at 25.9 % of aerosol mass as described in text. Remaining trace components shown are from Table 13 diluted by a factor of 1.14 to account for the effect of the increase in lead salts present when the effective mass emission rate went from 211.4 mg/mile in Table 13 to 241.4 mg/mile in this case.

(c) Composite of near-freeway leaded auto profile (weighted as 1.14 x 34446 kg/day), unleaded auto profile (weighted 787 kg/day), diesel profile (weighted 7736 kg/day), tire dust profile (weighted 6023 kg/day), and brake dust profile (weighted 7712 kg/day)

# CHAPTER 5

## RECEPTOR MODEL RESULTS

The chemical element balance described by equation (1) was evaluated for calendar year 1976 at each SCAQMD and NASN monitoring site studied. A separate chemical element balance calculation was undertaken for each daily filter sample at the SCAQMD stations and for each quarterly composite sample at the NASN sites. The contribution, $S_j$, of crustal material, highway aerosol, fuel oil fly ash, sulfates and nitrates was determined from equation (1) using a linear combination of the source profiles (the $f_{ij}a_{ij}$'s) appearing in Table 9. (The only exception was at the Lennox site where the HIGHWAY profile from Table 16 was used). Following the practice of previous investigators, source profiles were fit to the ambient concentrations of the most sensitive major tracer components: Pb, Fe, Mn, Ni, $SO_4^=$ and $NO_3^-$ at the SCAQMD sites and Pb, Fe, Mn, V, $SO_4^=$ and $NO_3^-$ at the NASN stations. A weighted least squares fitting procedure was used in which the ambient concentrations were weighted by $1/\sigma^2$, where $\sigma$ is an estimate of the standard deviation of a single determination of each ambient trace species concentration. A weighting or normalization scheme is necessary if the low concentration species, like manganese, are to influence the least squares fit.

The absolute accuracy and precision of the SCAQMD trace metals monitoring procedure is not known. Results published by Kniep et al. (1970) for atomic absorption analysis of ambient aerosol samples by similiar procedures would indicate a value of $\sigma$ equal to about 10% of the concentrations reported. That estimate for $\sigma$ was used in our

calculations. It is felt to be conservative. Communications with SCAQMD personnel (Wadley and Witz, 1981) indicate that if a formal error analysis were performed on the SCAQMD sampling protocol, the estimate for $\sigma$ obtained might be less than 5% of reported concentrations.

Chemical element balance results first were computed using the soil dust profile of Table 9 to represent crustal material. Source contributions in that case are given in the far left column of Figures 14 through 23. Values shown are annual averages in micrograms per cubic meter for the year 1976. Chemical element balance results for each daily or quarterly sample during that year are tabulated in Appendix D.

On the average, about 80% of the aerosol material present at the SCAQMD and NASN monitoring stations can be assigned to soil dust, highway aerosol, sulfates, nitrates and fuel oil fly ash by the chemical element balance. Highway aerosol accounts for about 20% of the TSP at most monitoring sites, with the exception of Azusa and San Bernardino which are lower (about 11% of TSP from highway aerosol).

Fuel oil fly ash constitutes about 1% of the aerosol at most SCAQMD sites, except for Lennox which is enriched in the oil ash component. This is not surprising since the Lennox monitoring site is located immediately inland from two large oil and gas fired power plants and an oil refinery. The relatively high oil ash estimate at the NASN sites are due to the use of vanadium as a tracer for oil ash. As mentioned previously, there are other significant vanadium sources

FIGURE 14

# DOWNTOWN LOS ANGELES AQMD MONITORING STATION AEROSOL SOURCE ASSIGNMENT FOR THE YEAR 1976

## (111.29 $\mu gm^{-3}$ TSP)

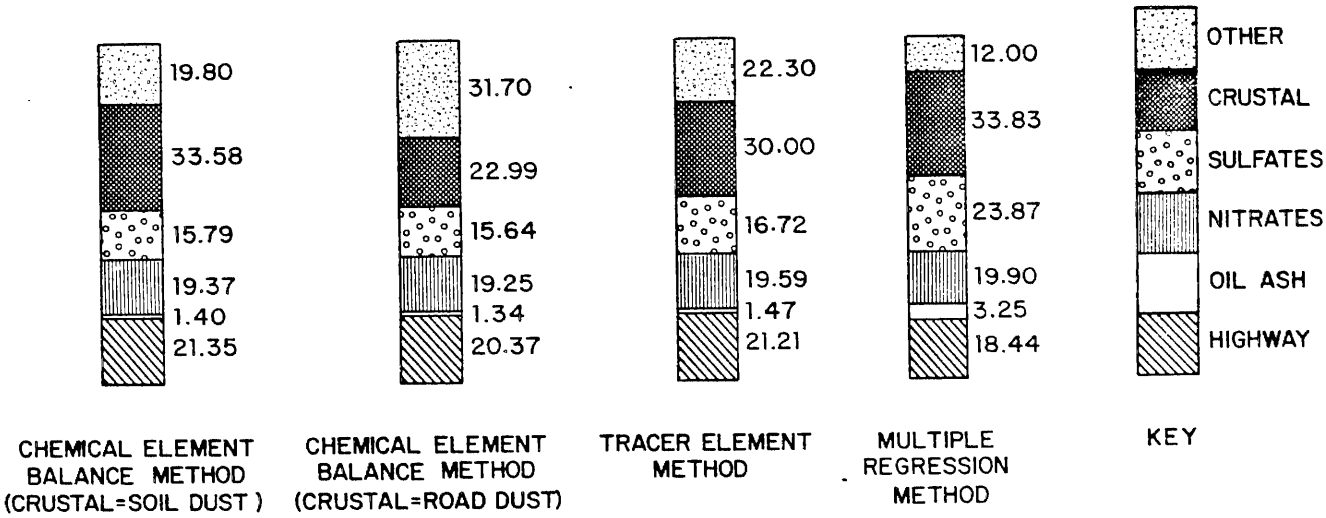


FIGURE 15

# LENNOX MONITORING STATION
# AEROSOL SOURCE ASSIGNMENT FOR THE YEAR 1976
# (102.41 $\mu gm^{-3}$ TSP)

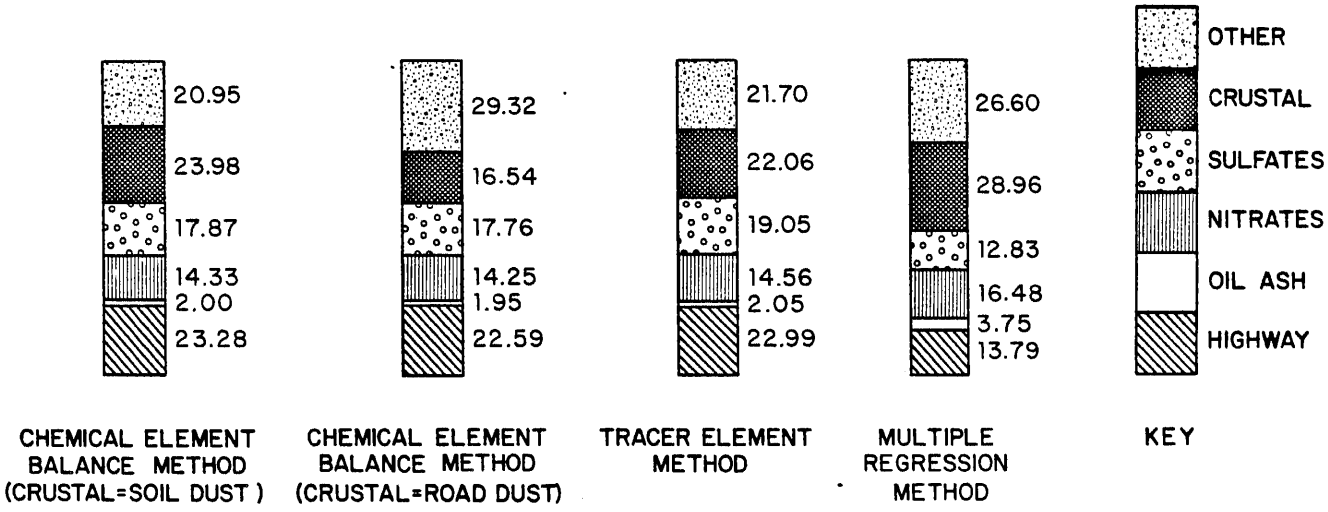


FIGURE 16

# WEST LOS ANGELES AQMD MONITORING STATION AEROSOL SOURCE ASSIGNMENT FOR THE YEAR 1976

## ( 70.40 $\mu gm^{-3}$ TSP )

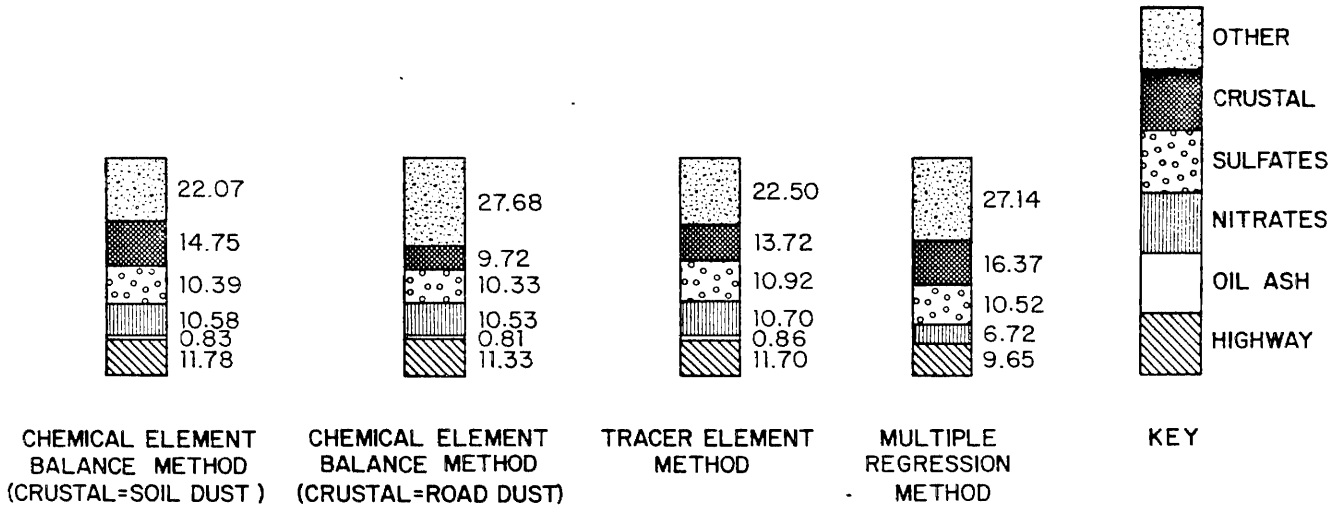


FIGURE 17

# RESEDA AQMD MONITORING STATION
# AEROSOL SOURCE ASSIGNMENT FOR THE YEAR 1976
# ( 97.63 $\mu gm^{-3}$ TSP )

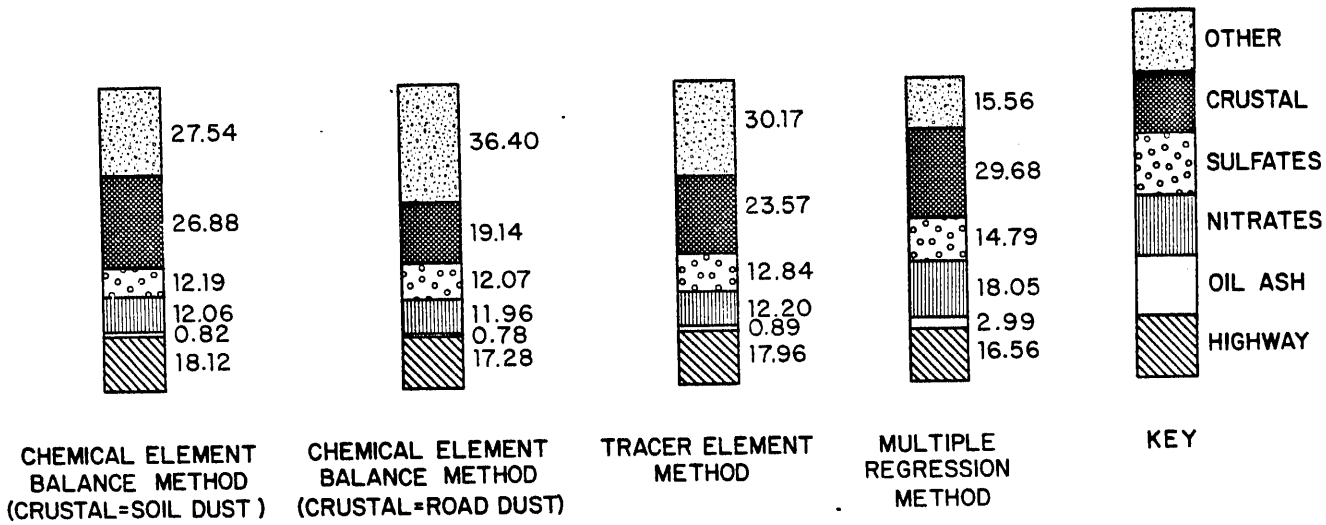


FIGURE 18

# LYNWOOD AQMD MONITORING STATION
# AEROSOL SOURCE ASSIGNMENT FOR THE YEAR 1976
# (116.25 $\mu gm^{-3}$ TSP)

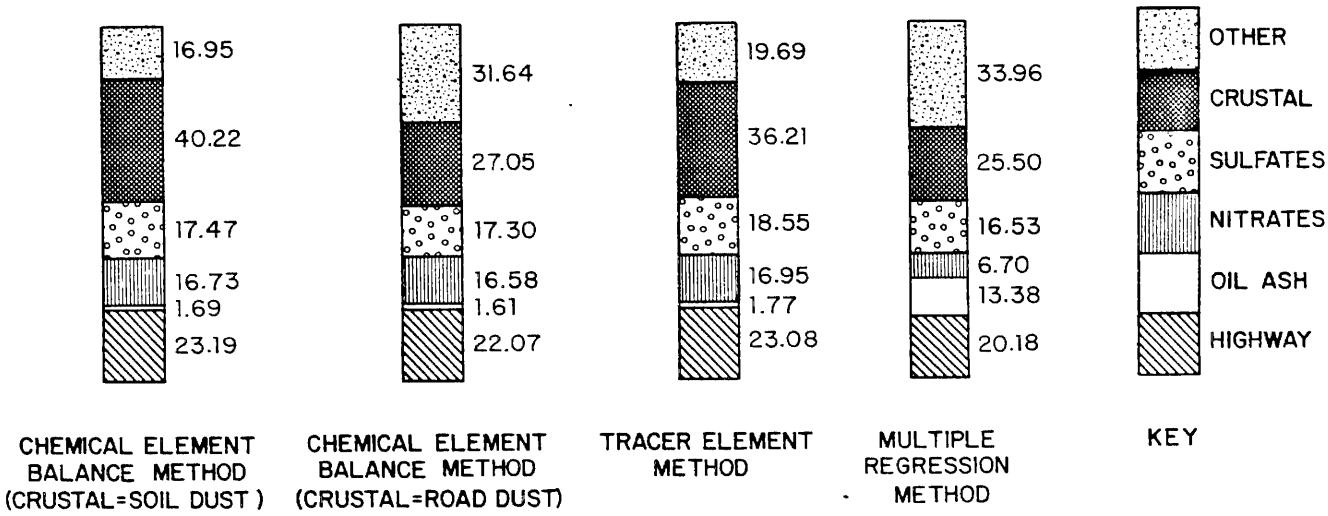


FIGURE 19

# PASADENA AQMD MONITORING STATION
# AEROSOL SOURCE ASSIGNMENT FOR THE YEAR 1976
# (101.70 $\mu gm^{-3}$ TSP)

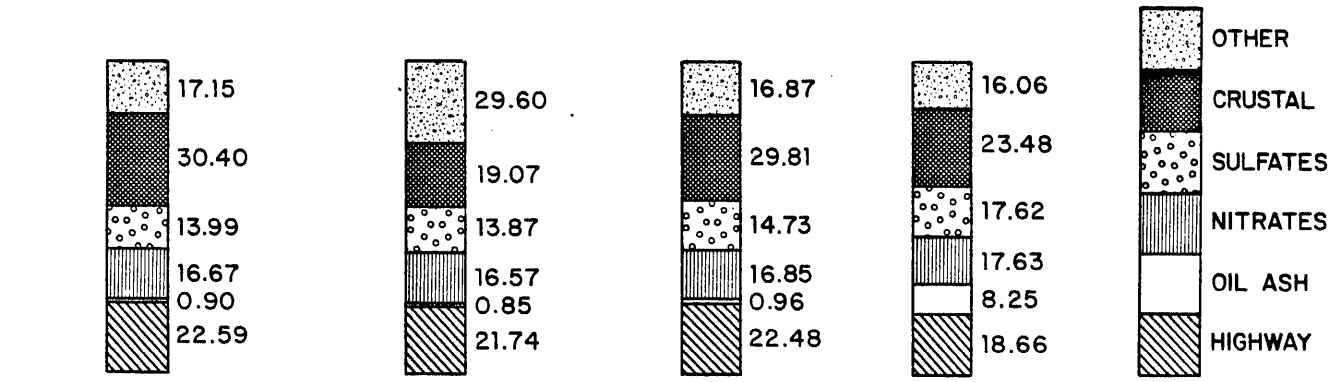


FIGURE 20

# AZUSA AQMD MONITORING STATION
# AEROSOL SOURCE ASSIGNMENT FOR THE YEAR 1976
# (119.16 $\mu gm^{-3}$ TSP)

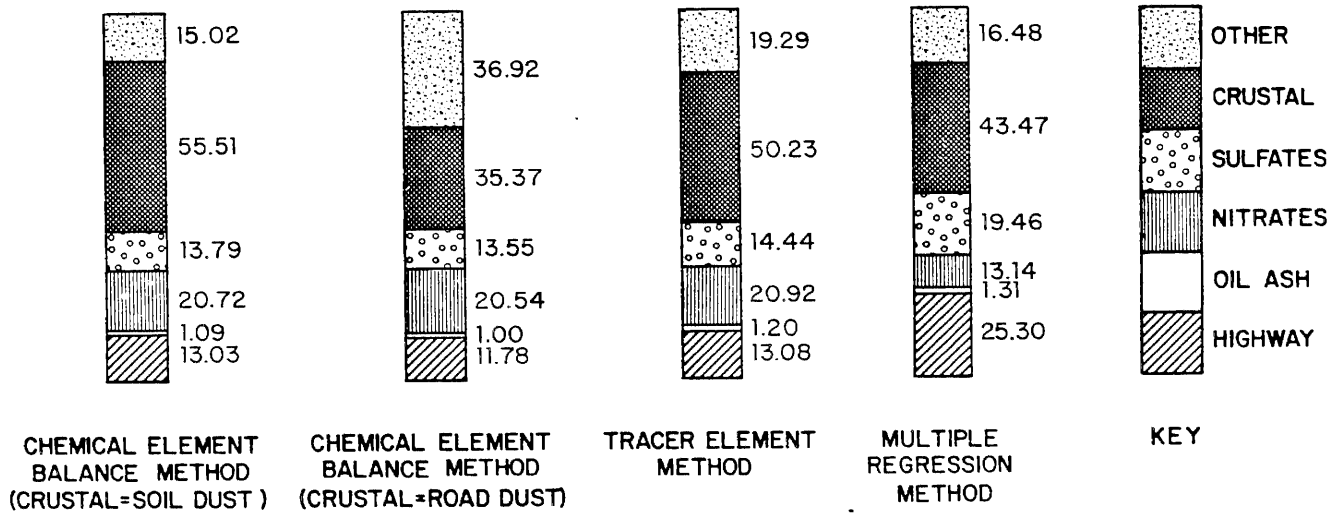


FIGURE 21

# DOWNTOWN LOS ANGELES NASN MONITORING STATION AEROSOL SOURCE ASSIGNMENT FOR THE YEAR 1976

## ( 109.00 $\mu gm^{-3}$ TSP )

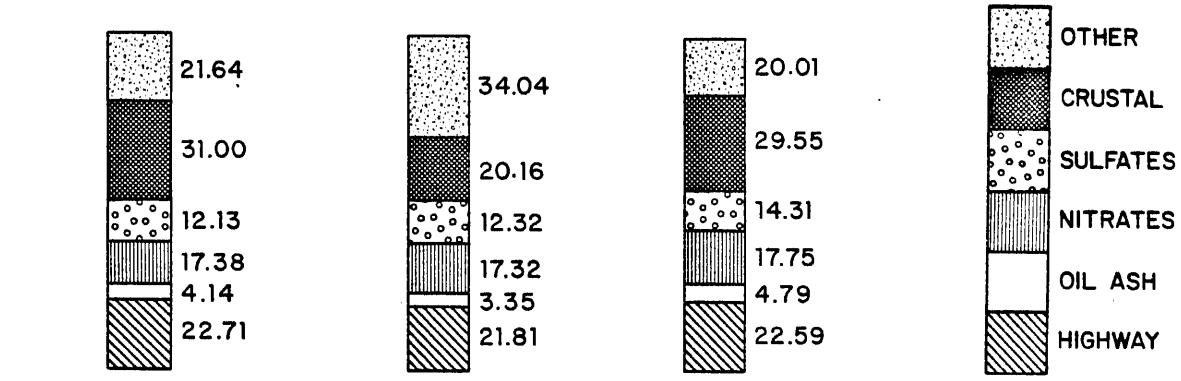


FIGURE 22

# ANAHEIM NASN MONITORING STATION
# AEROSOL SOURCE ASSIGNMENT FOR THE YEAR 1976
## ( 99.05 $\mu gm^{-3}$ TSP )

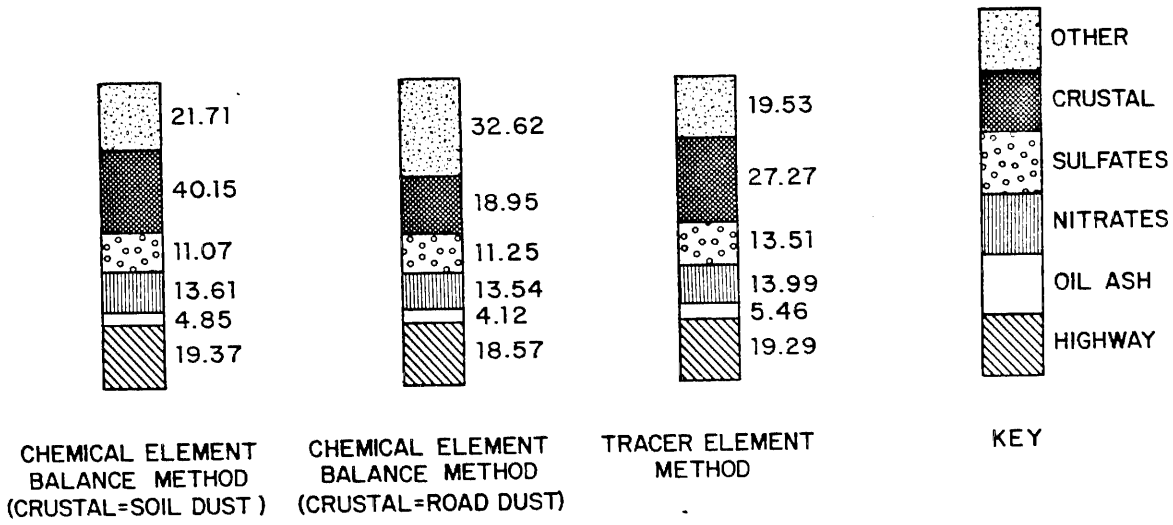
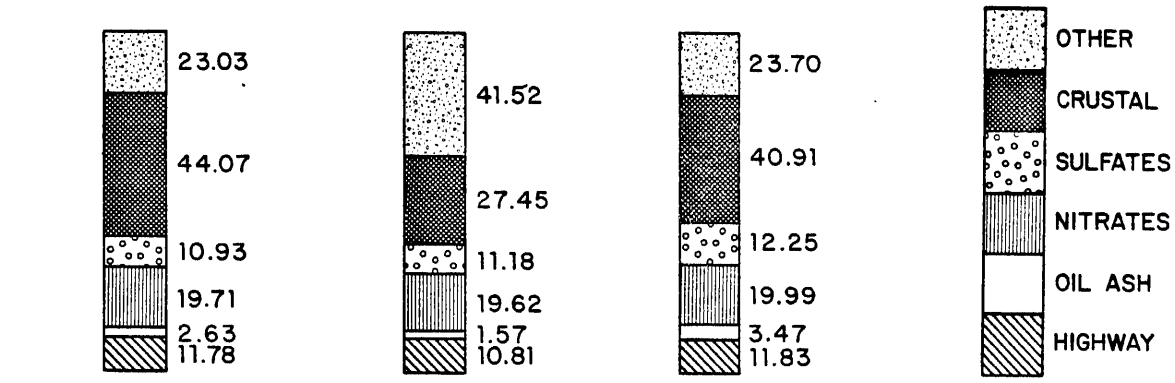


FIGURE 23

# SAN BERNARDINO NASN MONITORING STATION AEROSOL SOURCE ASSIGNMENT FOR THE YEAR 1976

## ( 112.15 $\mu gm^{-3}$ TSP )



in Los Angeles not included in these calculations; oil ash estimates at NASN stations are probably too high. Sulfates and nitrates are each present at about 14% to 15% of the total aerosol mass.

Soil dust-like material is the only component that varies greatly from place to place as a fraction of the TSP. Crustal material concentrations are lowest near the coast at West Los Angeles and at Lennox, accounting for 21% and 23% of the total mass respectively. Downtown Los Angeles, Pasadena, and Reseda are estimated to encounter TSP containing about 30% soil derived material. At Lynwood and Anaheim soil dust is somewhat higher, circa 40%. Azusa and San Bernardino appear to be quite dusty.

The emission inventory results of Tables 3 - 6 suggest that dust from paved road travel is the largest single source of crustal material emitted to the Los Angeles atmosphere. Paved road dust is enriched relative to soil dust in metals like lead that are contributed from vehicle traffic. In order to test the sensitivity of the source assignments to the presence of metals-laden road dust, the chemical element balance calculations were repeated using the road dust profile given in Table 9 to represent crustal material.

Annual mean chemical element balance results with crustal material represented by road dust are shown in Figures 14 through 23 (second column from the left). Source assignments for each individual sampling event during 1976 are tabulated in Appendix D. Estimated source contributions from highway aerosol, oil ash, sulfates and nitrates are virtually unchanged from the soil dust case. Crustal

material concentration estimates are about one third lower when using the road dust profile than with the pure soil dust profile.

It is not yet obvious which of these two sets of crustal material estimates should be preferred. The road dust treatment is attractive because it in theory more closely represents the activity generating much of the crustal emissions. But it should be remembered that the particular road dust profile used here was obtained from experiments in Portland, Oregon, where soils and street conditions may differ from those in Los Angeles. Measurements of the size distribution and chemical composition of road dusts in Los Angeles are needed. Ambient air quality data on aluminum or silicon concentrations also would help to better define the crustal component concentrations. In spite of the fact that refinements are possible given better measurements, it is still clear from the present study that crustal material constitutes a large fraction of the Los Angeles area aerosol.

From Figures 14 and 21 it is possible to compare results obtained at downtown Los Angeles using data from independent SCAQMD and NASN air monitoring programs operated at the same location. Source assignments are almost identical, except for fuel oil fly ash which constitutes a small fraction of total mass in either case. This provides an important quality control check, and suggest that the SCAQMD and NASN data can be merged for receptor modeling purposes. Those figures also show that source assignments derived from both networks respond in a similiar fashion when the soil dust and road dust profiles are interchanged.

Source assignments based on the best fit to Fe, Mn, Pb, Ni, V, $SO_4^=$ and $NO_3^-$ concentrations were used to compute the expected concentrations of each trace species appearing in the ambient data base. Annual average values of observed and calculated trace metals concentrations are shown in Tables 17 through 19. Species that were used in the least squares fitting procedure show an extremely close match between observed and calculated concentrations. This is expected since the system of equations used is only slightly over-determined. Of the remaining elements, Ti and Cr balance to within about a factor of two when the road dust profile is used. Zinc concentrations are underestimated, as should be expected because most of the zinc sources identified by the emissions inventory are not included within the simple five source chemical species balance attempted here. Cadmium and cobalt concentrations in both observed and predicted data sets are so low that meaningful comparison is impossible. Measured copper concentrations are much higher than can be attributed to the sources studied, as expected since the SCAQMD high volume samplers have been shown to contaminate themselves with copper worn from their own electric motors (Radke et al., 1977). Measured ammonium ion concentrations from the NASN network are much lower than expected if sulfates and nitrates were present as ammonium sulfate and ammonium nitrate, respectively. Possible explanations include incomplete neutralization of sulfuric acid-like aerosols, artifact sulfates and nitrates bound to filter surfaces rather than than to ammonium ions, the presence of metal sulfate salts, or sampling errors in the measurement of ammonium ion.

TABLE 17

Chemical Element Balance Results: Soil Dust Case

Average of Observed and Calculated Elemental Concentrations

1976

| AQMD Monitoring Station | $SO_4^=$ | | $NO_3^-$ | | Fe | | Mn | | Ni | | Pb | | Cr | | Cu | | Zn | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | OBS | CALC. | OBS | CALC. | OBS | CALC. | OBS | CALC. | OBS | CALC. | OBS | CALC. | OBS | CALC. | OBS | CALC. | OBS | CALC. |
| Downtown LA | 12.12 | 12.12 | 15.19 | 15.19 | 1.72 | 1.16 | 0.033 | 0.038 | 0.031 | 0.031 | 2.72 | 2.74 | 0.014 | 0.002 | 0.24 | 0.03 | 0.21 | 0.04 |
| Lennox | 13.80 | 13.80 | 11.29 | 11.29 | 1.39 | 0.86 | 0.024 | 0.028 | 0.043 | 0.043 | 4.08 | 4.13 | 0.011 | 0.003 | 0.24 | 0.02 | 0.15 | 0.04 |
| West LA | 7.91 | 7.91 | 8.30 | 8.30 | 0.74 | 0.52 | 0.015 | 0.017 | 0.018 | 0.018 | 1.50 | 1.51 | 0.007 | 0.001 | 0.44 | 0.01 | 0.17 | 0.02 |
| Reseda | 9.30 | 9.30 | 9.45 | 9.45 | 1.62 | 0.93 | 0.026 | 0.031 | 0.019 | 0.019 | 2.30 | 2.33 | 0.011 | 0.001 | 0.20 | 0.02 | 0.13 | 0.03 |
| Lynwood | 13.44 | 13.44 | 13.14 | 13.14 | 2.01 | 1.38 | 0.040 | 0.046 | 0.037 | 0.037 | 2.95 | 2.98 | 0.013 | 0.002 | 0.26 | 0.03 | 0.20 | 0.04 |
| Pasadena | 10.68 | 10.68 | 13.06 | 13.06 | 1.39 | 1.06 | 0.033 | 0.035 | 0.020 | 0.020 | 2.88 | 2.90 | 0.011 | 0.001 | 0.17 | 0.03 | 0.13 | 0.04 |
| Azusa | 10.46 | 10.46 | 16.22 | 16.22 | 2.49 | 1.83 | 0.055 | 0.062 | 0.025 | 0.025 | 1.67 | 1.68 | 0.018 | 0.001 | 0.30 | 0.02 | 0.20 | 0.02 |

All units are $\mu g\ m^{-3}$

TABLE 18

Chemical Element Balance Results: Road Dust Case

Average of Observed and Calculated Elemental Concentrations

1976

| AQMD Monitoring Station | $SO_4^=$ | | $NO_3^-$ | | Fe | | Mn | | Ni | | Pb | | Cr | | Cu | | Zn | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | OBS | CALC. | OBS | CALC. | OBS | CALC. | OBS | CALC. | OBS | CALC. | OBS | CALC. | OBS | CALC. | OBS | CALC. | OBS | CALC. |
| Downtown LA | 12.12 | 12.12 | 15.19 | 15.19 | 1.72 | 1.67 | 0.033 | 0.033 | 0.031 | 0.031 | 2.72 | 2.72 | 0.014 | 0.011 | 0.24 | 0.03 | 0.21 | 0.06 |
| Lennox | 13.80 | 13.80 | 11.29 | 11.29 | 1.39 | 1.24 | 0.024 | 0.024 | 0.043 | 0.043 | 4.08 | 4.08 | 0.011 | 0.009 | 0.24 | 0.03 | 0.15 | 0.05 |
| West LA | 7.91 | 7.91 | 8.30 | 8.30 | 0.74 | 0.72 | 0.015 | 0.014 | 0.018 | 0.018 | 1.50 | 0.50 | 0.007 | 0.005 | 0.44 | 0.015 | 0.17 | 0.03 |
| Reseda | 9.30 | 9.30 | 9.45 | 9.45 | 1.62 | 1.39 | 0.026 | 0.027 | 0.019 | 0.019 | 2.30 | 2.30 | 0.011 | 0.009 | 0.20 | 0.024 | 0.13 | 0.05 |
| Lynwood | 13.44 | 13.44 | 13.14 | 13.14 | 2.01 | 0.96 | 0.040 | 0.039 | 0.037 | 0.037 | 2.95 | 2.95 | 0.013 | 0.013 | 0.26 | 0.031 | 0.20 | 0.06 |
| Pasadena | 10.68 | 10.68 | 13.06 | 13.06 | 1.39 | 1.40 | 0.033 | 0.027 | 0.020 | 0.020 | 2.88 | 2.87 | 0.011 | 0.009 | 0.17 | 0.028 | 0.13 | 0.05 |
| Azusa | 10.46 | 10.46 | 16.22 | 16.22 | 2.49 | 2.50 | 0.055 | 0.049 | 0.025 | 0.025 | 1.67 | 1.67 | 0.018 | 0.015 | 0.30 | 0.02 | 0.20 | 0.06 |

All units are $\mu g\ m^{-3}$

Table 19

Chemical Element Balance Results at NASN Stations

| NASN Monitoring Station | Average of Observed and Calculated Elemental Concentrations | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $SO_4^=$ | | $NO_3^-$ | | Fe | | Mn | | V | | Pb | |
| | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. |
| 1. Soil Dust Case | | | | | | | | | | | | |
| Downtown L.A. (1965-76) | 11.37 | 11.37 | 10.40 | 10.40 | 1.75 | 1.18 | 0.033 | 0.039 | 0.011 | 0.011 | 3.52 | 3.56 |
| Anaheim (1969-76) | 10.93 | 10.93 | 8.20 | 8.20 | 1.40 | 0.93 | 0.027 | 0.031 | 0.011 | 0.011 | 2.24 | 2.26 |
| San Bernardino (1969-76) | 12.22 | 12.22 | 14.56 | 14.56 | 2.36 | 1.71 | 0.050 | 0.058 | 0.009 | 0.009 | 1.50 | 1.50 |
| 1. Road Dust Case | | | | | | | | | | | | |
| Downtown L.A. (1965-76) | 11.37 | 11.37 | 10.40 | 10.40 | 1.75 | 1.69 | 0.033 | 0.033 | 0.011 | 0.011 | 3.52 | 3.52 |
| Anaheim (1969-76) | 10.93 | 10.93 | 8.20 | 8.20 | 1.40 | 1.36 | 0.027 | 0.027 | 0.011 | 0.011 | 2.24 | 2.24 |
| San Bernardino (1969-76) | 12.22 | 12.22 | 14.56 | 14.56 | 2.36 | 2.42 | 0.050 | 0.048 | 0.009 | 0.009 | 1.50 | 1.50 |

Table 19 (Continued)

Chemical Element Balance Results at NASN Stations

| NASN Monitoring Station | Average of Observed and Calculated Elemental Concentrations | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $NH_4^+$ | | Cr | | Cu | | Ti | | Cd | | Co | |
| | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. |
| 1. Soil Dust Case | | | | | | | | | | | | |
| Downtown L.A. (1965-76) | 1.06 | 6.84 | 0.013 | 0.003 | 0.089 | 0.031 | 0.06 | 0.13 | 0.0018 | 0.0006 | 0.00 | 0.002 |
| Anaheim (1969-76) | 0.78 | 6.09 | 0.006 | 0.004 | 0.125 | 0.021 | 0.08 | 0.11 | 0.0014 | 0.0006 | 0.00 | 0.002 |
| San Bernardino (1969-76) | 1.26 | 8.58 | 0.014 | 0.002 | 0.216 | 0.016 | 0.10 | 0.21 | 0.0022 | 0.0003 | 0.001 | 0.002 |
| 1. Road Dust Case | | | | | | | | | | | | |
| Downtown L.A. (1965-76) | 1.06 | 6.90 | 0.013 | 0.011 | 0.089 | 0.035 | 0.06 | 0.15 | 0.0018 | 0.0004 | 0.00 | 0.0008 |
| Anaheim (1969-76) | 0.78 | 6.13 | 0.006 | 0.010 | 0.125 | 0.023 | 0.08 | 0.12 | 0.0014 | 0.0004 | 0.00 | 0.0009 |
| San Bernardino (1969-76) | 1.26 | 8.65 | 0.014 | 0.014 | 0.216 | 0.022 | 0.10 | 0.23 | 0.0022 | 0.00004 | 0.001 | 0.00008 |

The ratio between observed and predicted elemental concentrations in the present study is compared to the results of other receptor modeling applications in Table 20. In spite of the limitations of the historical air monitoring data bases, the results obtained here fall into the middle of the accuracy range established by studies in which a custom measurement program was undertaken to obtain data designed to meet the specifications of a chemical element balance.

The ability of the chemical element balance results to track daily fluctuations in TSP levels was tested. Source contributions at SCAQMD stations from highway aerosols, oil ash, crustal material, sulfates and nitrates were summed on each day. Then the 1976 TSP data were regressed on the daily summation of source contributions assigned by the chemical element balances. As seen in Table 21, aerosol mass accounted for by major source types tracks TSP concentration changes closely with near unit slope and a correlation coefficient ranging from 0.80 to 0.93.

From the source profiles given in Table 9, it is quickly apparent that chemical element balance results for highway aerosol are driven by Pb concentrations, oil ash results are driven by nickel or vanadium, and crustal components are scaled to iron and maganese. This suggests that daily source contributions to TSP levels might be estimated almost as closely by using these metals as if they were unique tracers for

Table 20

Comparison of the Average Ratio[a] Between Observed and Calculated Elemental Concentrations from Chemical Element Balance Studies

| Species | Kowalczyk et al. (1978) | Gatz (1975) | Friedlander (1973) | Present Study: SCAQMD Data 1976 | | Present Study: NASN Data 1965-76 | |
|---|---|---|---|---|---|---|---|
| | | | | Soil Dust Case | Road Dust Case | Soil Dust Case | Road Dust Case |
| Al | 1.15 (b) | 1.0 (b) | 1.2 (b) | | | | |
| As | 1.2 (b) | 20.0 | | | | | |
| Ba | 1.4 | | 5.7 | | | | |
| Br | 2.6 | 1.1 | 1.1 | | | | |
| Ca | 2.8 | 1.0 (b) | 1.0 (b) | | | | |
| Cd | 2.1 | 38. | | | | 4.22 | (c) |
| Ce | 1.5 | | | | | | |
| Cl | 6.2 | 16. | 30. | | | | |
| Co | 1.1 | 1.3 | | | | (d) | (d) |
| Cr | 3.7 | 1.3 | | 9.17 | 1.22 | 4.15 | 1.28 |
| Cu | 1.9 | 1.5 | 25. | 14.76 (e) | 11.87 (e) | 7.44 (e) | 5.93 (e) |
| Fe | 1.06 (b) | 1.2 | 7.5 | 1.48 (b) | 1.21 (b) | 1.46 (b) | 1.03 (b) |
| Hg | | 470.0 | | | | | |
| I | 2.0 | | 1500. | | | | |
| K | 1.5 | 2.2 | 1.5 (b) | | | | |
| La | 1.2 | 2.8 | | | | | |
| Mg | 2.1 | 3.2 | 4.1 (b) | | | | |
| Mn | 1.2 (b) | 1.0 (b) | 2.1 | 1.14 (b) | 1.07 (b) | 1.16 (b) | 1.01 (b) |
| Na | 1.0 (b) | 2.7 | 1.1 (b) | | | | |
| Ni | 2.5 | 3.5 | | 1.00 (b) | 1.00 (b) | | |
| Pb | 1.01 (b) | 1.0 (b) | 1.0 (b) | 1.01 (b) | 1.00 (b) | 1.01 (b) | 1.00 (b) |
| Sb | 4.2 | | | | | | |
| Sc | 1.3 | 2.7 | | | | | |
| Se | 2.9 | | | | | | |
| Th | 1.0 | | | | | | |
| Ti | 1.0 | 11. | | | | 1.88 | 2.10 |
| V | 1.0 (b) | 1.0 (b) | 1.0 (b) | | | 1.00 (b) | 1.00 (b) |
| Zn | 1.0 (b) | 7.3 (b) | 7.5 (b) | 5.73 | 3.43 | | |

Footnotes for Table 20

(a) Ratio of observed/predicted or predicted/observed, which ever is larger. Results due to Gatz (1975) and Friedlander (1973) are as summarized by Kowalczyk et al. (1978). Data from the present study reflect the observed/predicted ratios computed from Tables 17, 18 and 19, which were then averaged over all monitoring sites.

(b) Included in least squares fitting procedure.

(c) Value would be 4.0 if one extreme data point were excluded, the value is 21.0 otherwise.

(d) Ratio cannot be computed since observations are below the detection limit.

(e) Observations known to be biased by copper worn from high volume sampler motors.

TABLE 21

Total Suspended Particulate Matter Observations
Regressed on 1976 Daily Values of Source Contributions
Accounted for by Chemical Element Balance

1976

A. Soil Dust Profile Used to Fit Crusted Material

| Station | Regression Equation | Correlation Coefficient |
|---|---|---|
| Downtown LA | AQMD TSP = 1.01 [Accounted] + 19.12 | 0.91 |
| Lennox | AQMD TSP = 0.97 [Accounted] + 23.03 | 0.93 |
| West LA | AQMD TSP = 1.00 [Accounted] + 22.04 | 0.83 |
| Reseda | AQMD TSP = 1.03 [Accounted] + 25.77 | 0.80 |
| Lynwood | AQMD TSP = 0.67 [Accounted] + 49.63 | 0.88 |
| Pasadena | AQMD TSP = 1.03 [Accounted] + 14.82 | 0.89 |
| Azusa | AQMD TSP = 0.94 [Accounted] + 21.04 | 0.84 |

B. Road Dust Used to Fit Crustal Material

| | | |
|---|---|---|
| Downtown LA | AQMD TSP = 1.22 [Accounted] + 14.32 | 0.93 |
| Lennox | AQMD TSP = 1.14 [Accounted] + 19.15 | 0.93 |
| West LA | AQMD TSP = 1.19 [Accounted] + 19.56 | 0.82 |
| Reseda | AQMD TSP = 1.20 [Accounted] + 24.44 | 0.80 |
| Lynwood | AQMD TSP = 0.81 [Accounted] + 48.05 | 0.89 |
| Pasadena | AQMD TSP = 1.31 [Accounted] + 7.17 | 0.88 |
| Azusa | AQMD TSP = 1.33 [Accounted] + 9.63 | 0.91 |

their major source:

$$TSP_j = SULFATES_j + NITRATES_j + CRUSTAL_j + OIL\ ASH_j + HIGHWAY_j + OTHER_j \quad (9)$$

where the newly introduced terms are:

$TSP_j$ the total suspended particulate matter concentration on day j.

$OTHER_j$ the contribution to $TSP_j$ due to as yet unidentified sources.

Substituting equations (2), (3), (4), (5), and (7) into equation (9), we get for most SCAQMD stations:

$$TSP_j = 1.38\ SO_{4_j}^{=} + 1.29\ NO_{3_j}^{-} + 909.1\ Mn_j + 47.2\ Ni_j + 7.81\ Pb_j + OTHER_j \quad (10)$$

At Lennox, the corresponding expression is obtained by substitution from equations (2), (3), (4), (5) and (8):

$$TSP_j\ [Lennox] = 1.38\ SO_{4_j}^{=} + 1.29\ NO_{3_j}^{-} + 909.1\ Mn_j + 47.2\ Ni_j + 5.65\ Pb_j + OTHER_j \quad (11)$$

The NASN stations are similarly represented by:

$$TSP_j\ [NASN] = 1.38\ SO_{4_j}^{=} + 1.29\ NO_{3_j}^{-} + 909.1\ Mn_j + 255\ V_j + 7.81\ Pb_j + OTHER_j \quad (12)$$

Results of this tracer analysis at each monitoring site during 1976 are given in the third column from the left in Figures 14 through 23. The annual mean source assignments are very similar to the

chemical element balance calculations that used soil dust to represent crustal components. Source assignments by the tracer method are given in Appendix D for each daily or quarterly sampling event during 1976, and long-term means defined over the entire multi-year span of each monitoring station's data base are tabulated.

A stringent test of our tracer assignment is now possible. A statistical model is formulated in which the stoichiometric coefficients in equations (10), (11) and (12) are to be estimated by least squares regression of total suspended particulate matter concentration on sulfate, nitrate, manganese, nickel, and lead data. The regression model at SCAQMD stations is:

$$TSP_j = \beta_{SO_4} \cdot SO_{4_j} + \beta_{NO_3} \cdot NO_{3_j} + \beta_{CRUSTAL} \cdot Mn_j + \beta_{OIL} \cdot Ni_j + \beta_{HIGHWAY} \cdot Pb_j + \beta_{OTHER} + \varepsilon_j \qquad (13)$$

where

The $\beta$'s are undetermined stoichiometric coefficients that will be estimated by ordinary least squares regression analysis, and which are expected a priori to approximate the coefficients in equations (10) through (12).

$\varepsilon_j$ is the daily residual difference between estimated and observed total suspended particulate concentrations on each day, j.

The SCAQMD air quality data base at Downtown Los Angeles was applied to the multiple regression model of equation (13). As shown in Table 22, remarkably good agreement is obtained between our prior expectations and the coefficients estimated by least squares regression

TABLE 22

Chemically Resolved Regression Model Relating Tracer Element Concentrations to Pollutant Sources at Downtown Los Angeles

MODEL STRUCTURE:

$$TSP_j = SULFATES_j + NITRATES_j + CRUSTAL_j + OIL\ ASH_j + HIGHWAY_j + OTHER_j$$

MODEL ESTIMATED:

$$TSP_j = \beta_{SO_4} \cdot SO_4{}^{=}_j + \beta_{NO_3} \cdot NO_3{}^{-}_j + \beta_{CRUSTAL} \cdot Mn_j + \beta_{OIL} \cdot Ni_j + \beta_{HIGHWAY} \cdot Pb_j + \beta_{OTHER} + \varepsilon_j$$

| REGRESSION MODEL RESULTS | TSP AVERAGE (TSP VARIANCE) | COEFFICIENTS (STANDARD ERROR) | | | | | | CORRELATION COEFFICIENT (number of samples) |
|---|---|---|---|---|---|---|---|---|
| | | $\beta_{SO_4}$ | $\beta_{NO_3}$ | $\beta_{CRUSTAL}$ | $\beta_{OIL}$ | $\beta_{HIGHWAY}$ | $\beta_{OTHER}$ | |
| [1965-1977] | 140.83 | 1.85 | 1.24 | 958.5 | 69.6 | 7.12 | 29.16 | 0.84 |
| | (3546.2) | (0.11) | (0.15) | (47.9) | (41.5) | (0.52) | (2.86) | (742) |
| Prior Expectation | | 1.02 to 1.38 | 1.29 | 729.9 to 909.1 | 47.17 | 7.81 | | |

analysis of the historical data base. All coefficient estimates are statistically different from zero with greater than 95% confidence. Furthermore, with the exception of sulfates (which may be influenced by retained water), the stoichiometric coefficients estimated by regression analysis are statistically indistinguishable from the prior estimates made in equation (10) on the basis of source chemical composition and suspected origin. This provides support to the notion that lead in fact is acting as a tracer for a collection of vehicular sources, as hypothesized in our HIGHWAY profile, and that the mass fraction lead in that composite profile was estimated correctly. Even with the source of a large quantity of particulate matter remaining to be determined, the correlation between the summation of the identified source contributions and the measured total suspended particulate matter is 0.84 over the entire period 1965-1977. The regression model of equation (13) also was applied to the other SCAQMD stations, with similar results, as shown in Appendix D.

Iron is an alternative tracer for soil dust. Iron was substituted for manganese in equations (10) through (13) and the multiple regression model was recomputed. Results at Downtown Los Angeles are shown in Table 23, findings at other monitoring sites are tabulated in Appendix D. Regression analysis of the SCAQMD data suggests that iron is present as about 5% of crustal material mass giving a stoichiometric coefficient of $\beta_{CRUSTAL}$ equal to about 20. That value falls halfway between the iron content of the soil dust and the road dust profiles.

TABLE 23

Chemically Resolved Regression Model Relating Tracer Element Concentrations to Pollutant Sources at Downtown Los Angeles AQMD Station

MODEL STRUCTURE:

$$TSP_j = SULFATES_j + NITRATES_j + CRUSTAL_j + OIL\ ASH_j + HIGHWAY_j + OTHER_j$$

MODEL ESTIMATED:

$$TSP_j = \beta_{SO_4} \cdot SO_{4_j}^{=} + \beta_{NO_3} \cdot NO_{3_j}^{-} + \beta_{CRUSTAL} \cdot Fe_j + \beta_{OIL} \cdot Ni_j + \beta_{HIGHWAY} \cdot Pb_j + \beta_{OTHER} + \varepsilon_j$$

| REGRESSION MODEL RESULTS | TSP AVERAGE (TSP VARIANCE) | COEFFICIENTS (STANDARD ERROR) | | | | | | CORRELATION COEFFICIENT (number of samples) |
|---|---|---|---|---|---|---|---|---|
| | | $\beta_{SO_4}$ | $\beta_{NO_3}$ | $\beta_{CRUSTAL}$ | $\beta_{OIL}$ | $\beta_{HIGHWAY}$ | $\beta_{OTHER}$ | |
| [1965-1977] | 140.83 | 1.97 | 1.31 | 19.62 | 104.2 | 6.79 | 28.66 | 0.84 |
| | (3546.2) | (0.11) | (0.15) | (1.04) | (42.2) | (0.54) | (2.95) | (742) |
| Prior Expectation | | 1.02 to 1.38 | 1.29 | 14.45 to 31.25 | 47.17 | 7.81 | | |

Multiple regression model results at the Downtown Los Angeles NASN station are shown for comparison in Tables 24 and 25. Most coefficient estimates are still within two standard errors of our prior expectations, but those error bounds are much wider than at the SCAQMD sites. $\beta_{OIL}$ at the NASN sites in some cases is negative, again suggesting that vanadium is not as good a tracer for oil ash as nickel in Los Angeles.

Source contributions at SCAQMD sites during the year 1976 were synthesized from the multiple regression model application in which iron was used to represent crustal material. Annual mean results are given in the right hand column of Figures 14 through 20.

An analysis of the origin of Los Angeles peak pollutant episodes also was conducted at SCAQMD sites using the simple tracer method of equations (10) and (11). All 24-hour hi-vol samples of record from 1965-1977 with TSP levels above 350 micrograms per cubic meter are examined in Table 26. Several of these high TSP samples apparently are due to a dust storm that occurred on August 20, 1973. But on other occasions, like January 25, 1971 at Downtown Los Angeles, sulfates, nitrates and vehicle exhaust aerosol combined totaled more than 200 micrograms per cubic meter.

TABLE 24

Chemically Resolved Regression Model Relating Tracer Element Concentrations to Pollutant Sources at Downtown Los Angeles NASN Station

MODEL STRUCTURE:

$$TSP_j = SULFATES_j + NITRATES_j + CRUSTAL_j + OIL\ ASH_j + HIGHWAY_j + OTHER_j$$

MODEL ESTIMATED:

$$TSP_j = \beta_{SO_4} \cdot SO_{4_j}^{=} + \beta_{NO_3} \cdot NO_{3_j}^{-} + \beta_{CRUSTAL} \cdot Mn_j + \beta_{OIL} \cdot V_j + \beta_{HIGHWAY} \cdot Pb_j + \beta_{OTHER} + \ j$$

| REGRESSION MODEL RESULTS | TSP AVERAGE (TSP VARIANCE) | COEFFICIENTS (STANDARD ERROR) | | | | | | CORRELATION COEFFICIENT (number of quarters) |
|---|---|---|---|---|---|---|---|---|
| | | $\beta_{SO_4}$ | $\beta_{NO_3}$ | $\beta_{CRUSTAL}$ | $\beta_{OIL}$ | $\beta_{HIGHWAY}$ | $\beta_{OTHER}$ | |
| [1966-1976] | 119.42 | 2.74 | 1.76 | 1119.7 | -146.51 | 3.87 | 20.63 | 0.70 |
| | (916.51) | (0,76) | (0.83) | (346.10) | (279.9) | (2.46) | (15.12) | (38) |
| Prior Expectation | | 1.02 to 1.38 | 1.29 | 729.9 to 909.1 | 295.0 | 7.81 | | |

TABLE 25

Chemically Resolved Regression Model Relating Tracer Element Concentrations to Pollutant Sources at Downtown Los Angeles NASN Station

MODEL STRUCTURE:

$$TSP_j = SULFATES_j + NITRATES_j + CRUSTAL_j + OIL\ ASH_j + HIGHWAY_j + OTHER_j$$

MODEL ESTIMATED:

$$TSP_j = \beta_{SO_4} \cdot SO_{4_j}^{=} + \beta_{NO_3} \cdot NO_{3_j}^{-} \cdot \beta_{CRUSTAL} \cdot Fe_j + \beta_{OIL} \cdot V_j \cdot \beta_{HIGHWAY} \cdot Pb_j + \beta_{OTHER} + \varepsilon_j$$

| REGRESSION MODEL RESULTS | TSP AVERAGE (TSP VARIANCE) | COEFFICIENTS (STANDARD ERROR) | | | | | | CORRELATION COEFFICIENT (number of quarters) |
|---|---|---|---|---|---|---|---|---|
| | | $\beta_{SO_4}$ | $\beta_{NO_3}$ | $\beta_{CRUSTAL}$ | $\beta_{OIL}$ | $\beta_{HIGHWAY}$ | $\beta_{OTHER}$ | |
| [1969-1977] | 119.42 | 2.87 | 1.39 | 34.79 | 42.18 | 0.88 | 8.05 | 0.77 |
| | (916.51) | (0.68) | (0.75) | (7.33) | (256.67) | (2.41) | (14.13) | (38) |
| Prior Expectation | | 1.02 to 1.38 | 1.29 | 14.45 to 31.25 | 295.0 | 7.81 | | |

TABLE 26

Analysis of Peak Pollutant Episodes

Total Suspended Particulate Matter $\geq$ 350 $\mu g\ m^{-3}$

(By Tracer Element Method)

| Location | Date | TSP | Sulfates | Nitrates | Highway | Crustal | Oil Ash | Other |
|---|---|---|---|---|---|---|---|---|
| Downtown LA | 12/17/69 | 371.0 | 37.95 | 35.86 | 55.42 | 72.73 | 4.25 | 164.80 |
| Downtown LA | 1/25/71 | 384.5 | 74.80 | 39.22 | 93.50 | 72.73 | 0.94 | 103.32 |
| Downtown LA | 8/20/73 | 412.0 | 16.56 | 0.52 | 36.03 | 236.37 | 3.77 | 118.75 |
| Downtown LA | 11/13/73 | 386.0 | 32.02 | 21.41 | 159.64 | 145.46 | 2.36 | 25.12 |
| Reseda | 10/29/69 | 467.0 | 2.48 | 6.58 | 53.36 | 72.73 | 0.94 | 330.90 |
| Reseda | 11/19/71 | 443.0 | 44.44 | 19.87 | 100.11 | 190.91 | 3.77 | 83.90 |
| Reseda | 3/23/72 | 608.0 | 95.77 | 11.61 | 117.67 | 209.09 | 2.83 | 171.02 |
| Reseda | 8/05/73 | 472.0 | 167.12 | 1.55 | 86.66 | 154.55 | 9.43 | 52.69 |
| Reseda | 8/20/73 | 536.0 | 37.12 | 11.35 | 45.61 | 300.00 | 4.25 | 137.67 |
| Pasadena | 8/20/73 | 624.0 | 16.84 | 12.77 | 25.09 | 363.64 | 3.30 | 202.37 |
| Azusa | 11/09/71 | 418.0 | 60.72 | 55.99 | 74.80 | 163.64 | 4.72 | 58.14 |
| Azusa | 8/20/73 | 686.0 | 10.63 | 12.13 | 15.96 | 372.73 | 2.83 | 271.72 |

All units are $\mu g\ m^{-3}$

# CHAPTER 6

## SUMMARY AND CONCLUSIONS

Trace metals concentrations in atmospheric particulate samples have been measured by the National Air Surveillance Network and by local air pollution control districts for many years. However, the number of trace metals determined usually is small, and important marker elements like aluminum and silicon from soil dust often are unmeasured. Nevertheless, these data sets can be used to identify the emissions sources contributing to air monitoring sites by chemical element balance or tracer techniques. The key is to employ emissions inventory data to assess the ability of those metals that were measured to act as tracers for major source types.

Aerosol source assignment methods that employ routine air monitoring data were tested in the Los Angeles area. An emissions inventory for fine particle trace metals ($d_p$ < 10 micron) in that air basin was constructed for the year 1976. It was found that over 80% of the fine lead emissions in that airshed came from highway traffic, 81% of the nickel was estimated to arise from fuel oil fly ash, 93% of the manganese came from soil-like materials, and 94% of the iron emitted likewise came from soil-like sources. These metals are measured as part of routine ambient sampling programs and should be able to act as nearly unique tracers for the presence of material from these major source types.

Chemical element balances were constructed at 10 Los Angeles area monitoring sites for the year 1976. The objective was to subdivide the

ambient aerosol at each monitoring site into contributions from highway vehicles, fuel oil fly ash, soil or road dust, sulfates and nitrates. It was found that about 80% of the particulate matter at each monitoring site could be attributed to the sum of those sources. Typically, most monitoring sites received about 20% of their aerosol mass from highway vehicles, 1% to 2% of total mass from fuel oil fly ash, while sulfates and nitrates were each present at circa 15% of total mass. Soil or road dust concentrations are lowest (about 22% of total mass) in the western coastal area of the South Coast Air Basin (at West Los Angeles). Airborne concentrations of soil like materials generally increase as one moves eastward towards Azusa and San Bernardino. The aerosol at Azusa in 1976 averaged nearly 50% soil-like crustal material. These crustal source assignments could be improved if data on the spatial distribution of the chemical composition of resuspended soil dust were available in Los Angeles.

Chemical element balance results were checked against multivariate statistical models that take advantage of the time series format and tremendous number of daily samples available within routine air monitoring data sets. Ambient total suspended particulate matter concentrations on each day were fit to a linear combination of the most prominent trace metals contributed by highway, fuel oil, and soil dust sources, plus sulfates and nitrates. The regression coefficients from that analysis were compared to the expected abundance of iron and manganese in soil, nickel in oil ash, and lead in highway vehicle aerosol. In most cases, the regression coefficients were statistically indistinguishable from the values expected, adding confirmation to the likely

accuracy of the source chemical composition data used in the chemical element balances.

Similar trace metals data from the National Air Surveillance Network and from state and local agencies are available at hundreds of sites throughout California and the United States. These data can be used to improve the accuracy of the source contribution estimates that form the basis for TSP emission control stategies.

## REFERENCES

Cass, G.R., Boone, P.M., Macias, E.S. (1981) "Emissions and Air Quality Relationships for Atmospheric Carbon Particles in Los Angeles," in Particulate Carbon: Atmospheric Life Cycle, G.T. Wolff and R.L. Klimisch eds., Plenum Press, New York, (In press).

Cass, G.R. (1975) Lead as a Tracer for Automotive Particulates: Projecting the Sulfate Air Quality Impact of Oxidation Catalyst Equipped Cars in Los Angeles, Pasadena, California, California Institute of Technology, Environmental Quality Laboratory Memorandum No. 12.

Dillard, C.R. and Goldberg, D.E. (1971) Chemistry-Reactions, Structure and Properties, Collier-MacMillian, Ltd., London, 654 pp.

Cooper, J.A. and Watson, J.G., Jr. (1980) "Receptor Oriented Methods of Air Particulate Source Apportionment," J. of the Air Pollution Control Association, 30, 1116-1130.

Faoro, R.B. and McMullen, T.B. (1977) National Trends in Trace Metals in Ambient Air 1965-1974, U.S. Environmental Protection Agency, Report No. EPA-450/1-77-003.

Friedlander, S.K. (1973) "Chemical Element Balances and Identification of Air Pollution Sources," Environmental Science and Technology, 7, 235-240.

Gartrell, G., Jr. and S.K. Friedlander (1975) "Relating Particulate Pollution to Sources: The 1972 California Aerosol Characterization Study," Atmospheric Environment, 9, 279-299.

Gatz, D.F. (1975) "Relative Contributions of Different Sources of Urban Aerosols: Application of a New Estimation Method to Multiple Sites in Chicago," Atmospheric Environment, 9, 1-18.

Gordon, G.E. (1980) "Receptor Models," Environmental Science and Technology, 14, 792-800.

Habibi, K. (1973) "Characterization of Particulate Matter in Vehicle Exhaust," Environmental Science and Technology, 7, 223-234.

Hammerle, R.H. and Pierson, W.R. (1975) "Sources and Elemental Composition of Aerosol in Pasadena, California, Energy-Dispersive X-Ray Fluorescence," Environmental Science and Technology, 9 1058-1068.

Hidy, G.M. et al. (1974) Characterization of Aerosols in California (ACHEX), Science Center, Rockwell International, prepared under California Air Resources Board Contract No. 358.

Hidy, G.M. and Friedlander S.K. (1970) "The Nature of the Los Angeles Aerosol," in Eglund, H.M. and Berry, W.T., eds., Proceedings Second International Clean Air Congress, Academic Press, New York.

Huntzicker, J.J., Friedlander, S.K. and Davidson, C.I. (1975) "Material Balance for Automobile-Emitted Lead in Los Angeles Basin," Environmental Science and Technology, 9, 448-457.

Kleinman, M.T., Pasternak, B.S., Eisenbud, M. and Kneip, T.J. (1980) "Identifying and Estimating the Relative Importance of Sources of Airborne Particulates," Environmental Science and Technology, 14, 62-65.

Kneip, T.J., Eisenbach, M., Strehlow, C.D. and Freudenthal, P.C. (1970), Airborne Particles in New York City, Journal of the Air Pollution Control Association, 20, 144-149.

Kneip, T.J., Kleinman, M.T. and Eisenbach, M. (1972) "Relative Contribution of Emission Sources to the Total Airborne Particulates in New York City," Proceedings of the 3rd IUAPPA Clean Air Congress, C96-C97.

Kowalczyk, G.S., Choquette, C.E. and Gordon, G.E. (1977) "Chemical Element Balances and Identification of Air Pollution Sources in Washington, D.C.," Atmospheric Environment, 12, 1143-1153.

Laresgoiti, A. and Springer, G.S. (1977) "Sulfate and Particulate Emissions from an Oxidation Catalyst Equipped Engine," Environmental Science and Technology, 11, 285-292.

Lynch, J.R. (1968) "Brake Lining Decomposition Products," J. Air Pollution Control Association, 18, 824-826.

Miller, M.S., Friedlander, S.K. and Hidy, G.M. (1972) "A Chemical Element Balance for the Pasadena Aerosol," J. Colloid and Interface Science, 39, 165-176.

Morton, M. ed. (1973) Rubber Technology, Litton Educational Publishing, New York, New York.

Muhlbaier, J.L. and Williams, R.L. (1981) "Fireplaces, Furnaces and Vehicles as Emissions Sources of Particulate Carbon," in Particulate Carbon: Atmospheric Life Cycle, G.T. Wolff and R.L. Klimisch eds., Plenum Press, New York.(In press)

Ondov, J.M. (1974) A Study of Trace Elements on Particulates From Motor Vehicles, Ph.D. Thesis, University of Maryland, (As cited by Kowalczyk et al. 1978)

Pierson, W.R. (1977) Ford Motor Company, Personal Communication, August 3.

Pierson, W.R. and W.W. Brachaczek (1974) "Airborne Particulate Debris from Rubber Tires," Rubber Chemistry and Technology, 47, 1275-1299

Pierson, W.R. and Brachaczek, W.W. (1976) Particulate Matter Associated with Vehicles on the Road, Society of Automotive Engineers Paper No. 760039.

Radke, N.M., Cherniack, I., Witz, S. and MacPhee, R.D. (1977) "The Effect of Type of Air sampler on Composition of Collected Particulates: A Comparison of Brushless and Brush-type Hi-vol Air Samplers," South Coast Air Quality Management District, Technical Services Division Report, El Monte, California, 18 pp.

Taback, H.J., Brienza, A.R., Macko, J. and Brunetz, N. (1979) "Fine Particle Emissions from Stationary and Miscellaneous Sources in the South Coast Air Basin," Report Number KVB 5806-783, KVB Inc., Tustin, California. (Profiles are contained in Appendix A)

U.S. Bureau of Mines (1966-1980) Motor Gasolines, Summer 1965, U.S. Department of the Interior, Mineral Industry Surveys, Petroleum Products Surveys No. 75. Series continues semi-annually. Later editions in this series are published by the U.S. Department of Energy.

U.S. Environmental Protection Agency (1972) Air Quality Data for 1968 from the National Air Surveillance Networks and Contributing State and Local Networks, U.S. Environmental Protection Agency Report No. APTD-0978. (Similar reports are available for other years)

Wadley, M.W. and MacPhee, R.D. (1976a) Measurements of Suspended Particulate Matter in the Atmosphere of Los Angeles County - 1965-1974 - A Ten-Year Summary, Southern California Air Pollution Control District, Technical Services Division Report 82.

Wadley, M.W. and MacPhee, R.D. (1976b) Suspended Particulate Matter in the Atmosphere of Los Angeles County - 1975, Southern California Air Pollution Control District, Technical Services Division Report 83.

Wadley, M.W., Schoenemann, K.H. and MacPhee, R.D. (1979a) Suspended Particulate Matter in the Atmosphere of the South Coast Air Basin and Southeast Desert Areas 1976, South Coast Air Quality Management District, Technical Services Division Air Quality Report No. 86.

Wadley, M.W., Schoenemann, K.H. and MacPhee, R.D. (1979b) Suspended Particulate Matter in the Atmosphere of the South Coast Air Basin and Southeast Desert Areas 1977, South Coast Air Quality Management District, Technical Services Division Air Quality Report No. 87.

Wadley, M.W. and Witz, S. (1981), South Coast Air Quality Management District, personal Communication.

White, W.H. and Roberts, P.T. (1977) "On the Nature and Origins of Visibility Reducing Aerosols in the Los Angeles Air Basin," Atmospheric Environment, 11, 803-812.

Watson, J. G. Jr. (1979) Chemical Element Balance Receptor Model Methodology for Assessing the sources of Fine and Total Suspended Particulate Matter in Portland, Oregon, Ph.D. Thesis, Oregon Graduate Center, Beaverton, Oregon.

# APPENDIX A

## DISPLAY OF PARTICULATE AIR QUALITY DATA AT DIFFERENT MONITORING SITES WITHIN THE SOUTH COAST AIR BASIN

### A.1 Introduction

Data on the chemical composition of airborne particulate matter in the Los Angeles area are presented graphically in this appendix. Ten monitoring sites are studied, at locations indicated on Figure A.1.1. The analysis periods and species studied are shown in Tables A.1.1, A.1.2 and A.1.3.

### A.2 Data Preparation

High volume sampler data on total suspended particulate concentrations, sulfates, nitrates and seven trace metals (Fe, Mn, Pb, Cr, Cu, Ni, Zn) were hand copied from the files of the South Coast Air Quality Management District (SCAQMD). The period covered was August 1965 through December 1977. If duplicate samples were available for a 24-hour period, then the arithmetic mean of the two observations was recorded. Filter samples taken prior to November 1969 were subjected to high temperature ashing before trace metals extraction with nitric acid. It was found that this procedure leads to volatilization of much of the lead collected. A study of the early lead data has been completed by the SCAQMD. They recommended that the lead concentrations measured prior to November 1969 be multiplied by 2.92 in order to recover concentrations equivalent to those obtained in recent years by

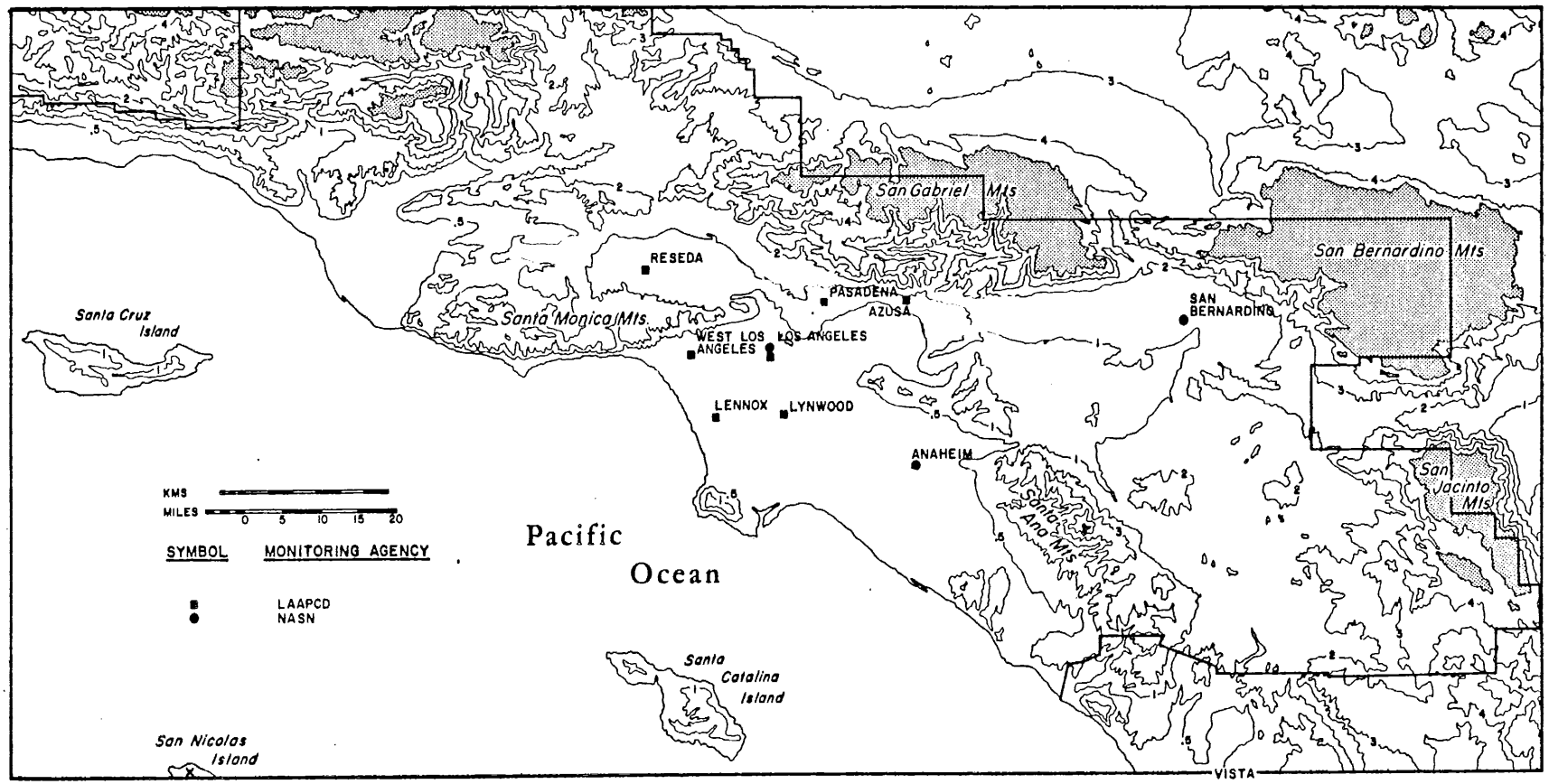



Figure A.1.1

Location of Particulate Monitoring Sites in the South Coast Air Basin

TABLE A.1.1

Monitoring Sites and Analysis Periods for Particulate Data Collected Within the South Coast Air Basin

| Monitoring Site | Analysis Period | Monitoring Agency | |
|---|---|---|---|
| | | NASN | SCAQMD |
| Azusa | Jul 1971 - Dec 1977 | | * |
| Downtown Los Angeles | Aug 1965 - Dec 1977 | | * |
| Lennox | Aug 1965 - Dec 1977 | | * |
| Lynwood | Jan 1974 - Dec 1977 | | * |
| Pasadena | Jul 1971 - Dec 1977 | | * |
| Reseda | Sep 1967 - Dec 1977 | | * |
| West Los Angeles | Aug 1965 - Dec 1977 | | * |
| Anaheim | 1969 - 1976 | * | |
| Downtown Los Angeles | 1965 - 1976 | * | |
| San Bernardino | 1969 - 1976 | * | |

Note: The NASN data are quarterly composites

TABLE A.1.2

Species Measured at NASN and SCAQMD Monitoring Sites

| Species | Symbol | Molecular Weight | Monitoring Agency | |
|---|---|---|---|---|
| | | | NASN | SCAQMD |
| Cadmium | Cd | 112.40 | * | |
| Chromium | Cr | 52.00 | * | * |
| Cobalt | Co | 58.93 | * | |
| Copper | Cu | 63.55 | * | * |
| Iron | Fe | 55.85 | * | * |
| Lead | Pb | 207.20 | * | * |
| Manganese | Mn | 54.94 | * | * |
| Nickel | Ni | 58.71 | | * |
| Tin | Sn | 118.69 | * | |
| Titanium | Ti | 47.90 | * | |
| Vanadium | V | 50.94 | * | |
| Zinc | Zn | 65.38 | | * |
| Sulfates | $SO_4^=$ | | * | * |
| Nitrates | $NO_3^-$ | | * | * |
| Ammonium Ion | $NH_4^+$ | | * | |
| TSP | | | * | * |

TABLE A.1.3

Summary of Data Displayed in this Appendix

| Monitoring Site | Monitoring Agency | | Figures | Tables |
|---|---|---|---|---|
| | NASN | SCAQMD | | |
| Azusa | | * | A.3.1 - A.3.20 | A.3.1 - A.3.2 |
| Downtown Los Angeles | | * | A.4.1 - A.4.20 | A.4.1 - A.4.2 |
| Lennox | | * | A.5.1 - A.5.20 | A.5.1 - A.5.2 |
| Lynwood | | * | A.6.1 - A.6.20 | A.6.1 - A.6.2 |
| Pasadena | | * | A.7.1 - A.7.20 | A.7.1 - A.7.2 |
| Reseda | | * | A.8.1 - A.8.20 | A.8.1 - A.8.2 |
| West Los Angeles | | * | A.9.1 - A.9.20 | A.9.1 - A.9.2 |
| Anaheim | * | | A.10.1 - A.10.20 | A.10.1 - A.10.2 |
| Downtown Los Angeles | * | | A.11.1 - A.11.20 | A.11.1 - A.11.2 |
| San Bernardino | * | | A.12.1 - A.12.20 | A.12.1 - A.12.2 |

Note: The NASN data are quarterly composites

direct nitric acid extraction. This correction factor has been used in the present study.

Trace metals data are graphed in time series at each SCAQMD station in sections A.3 through A.9 of this appendix. For each chemical species of interest, two graphs are presented. The upper graph of each pair shows the raw air quality data and is useful for locating peak pollutant concentrations. In order to better expose concentration trends over time, a second figure is presented in which the time series of air quality data have been passed through a linear digital filter. This filtering procedure smooths out concentration fluctuations with frequency greater than four cycles per year leaving seasonal trends intact.

Air quality data from the National Air Surveillance Network (NASN) monitoring sites at Downtown Los Angeles, Anaheim and San Bernardino are graphed in sections A.10 through A.12 of this appendix. NASN trace metals data, plus sulfates, nitrates and ammonium ion data were provided through the assistance of Gerald Akland of the U.S. Environmental Protection Agency (printouts dated November 21-24, 1978). NASN total suspended particulate matter data from years prior to 1975 were provided by the U.S. Environmental Protection Agency on punched cards in SAROAD format. NASN total suspended particulate data for the years 1975 and 1976 were copied from records maintained by the California Air Resources Board. Sulfates, nitrates, ammonium ion and TSP data were available for single 24-hour periods, while the NASN trace metals data were reported as four quarterly averages for each year. The daily TSP,

$SO_4^=$ and $NO_3^-$ data thus were averaged over each quarter year before use in order to place them into the same time frame as the trace metals data base. The NASN data are graphed in histogram form to show this quarterly averaging process accurately.

## A.3 Monitoring Data at Azusa Site (SCAQMD)

TABLE A.3.1

Particulate Data Available at Azusa Monitoring Site (SCAQMD)

| Chemical Species | Figures[a] |
|---|---|
| Chromium | A.3.1 - A.3.2 |
| Copper | A.3.3 - A.3.4 |
| Iron | A.3.5 - A.3.6 |
| Lead | A.3.7 - A.3.8 |
| Manganese | A.3.9 - A.3.10 |
| Nickel | A.3.11 - A.3.12 |
| Zinc | A.3.13 - A.3.14 |
| Sulfates | A.3.15 - A.3.16 |
| Nitrates | A.3.17 - A.3.18 |
| Total Suspended Particulate | A.3.19 - A.3.20 |

a Odd numbered figures correspond to measured data and even numbered ones to filtered results.

TABLE A.3.2

Summary of Particulate Air Quality Statistics
at Azusa Monitoring Site (SCAQMD)
(Jul 1971 - Dec 1977)

| Chemical Species | Number of Samples | Statistics | | |
|---|---|---|---|---|
| | | Mean | Maximum | Minimum |
| | | (Micrograms $m^{-3}$) | | |
| Chromium | 406 | 0.021 | 0.090 | 0.00 |
| Copper | 402 | 0.31 | 6.08 | 0.01 |
| Iron | 386 | 3.12 | 26.45 | 0.00 |
| Lead | 432 | 2.18 | 9.58 | 0.00 |
| Manganese | 432 | 0.077 | 0.41 | 0.00 |
| Nickel | 401 | 0.032 | 1.92 | 0.00 |
| Zinc | 407 | 0.29 | 8.80 | 0.00 |
| Sulfates | 434 | 12.15 | 55.70 | 0.10 |
| Nitrates | 434 | 12.60 | 71.70 | 0.20 |
| TSP | 434 | 139.71 | 686.00 | 10.00 |

Note: All samples are 24 hour averages

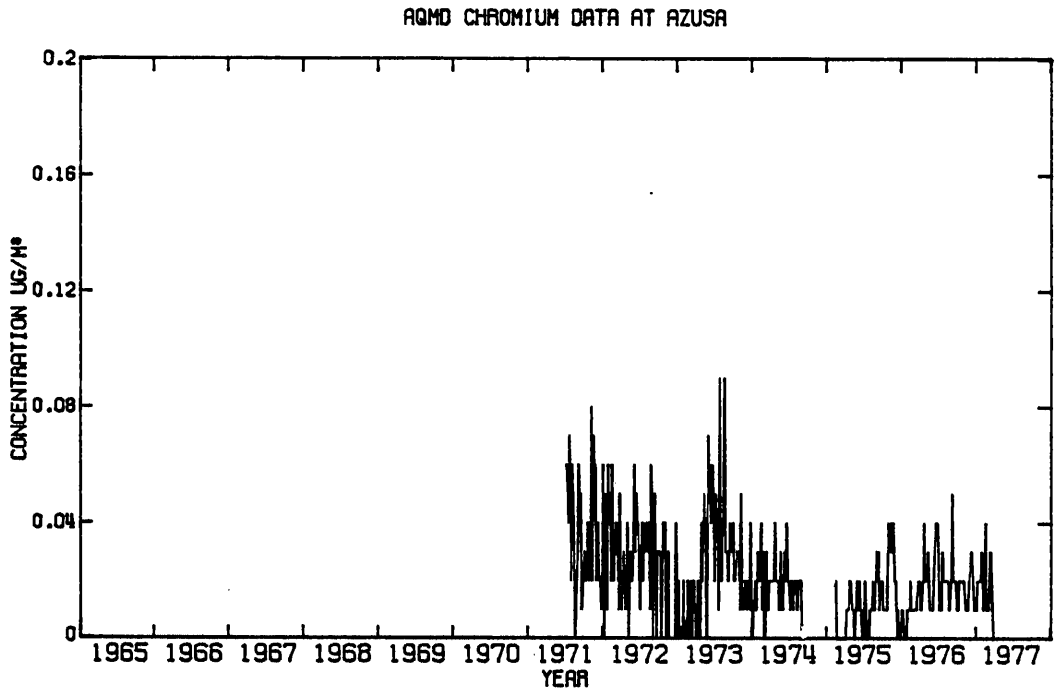



FIGURE A.3.1

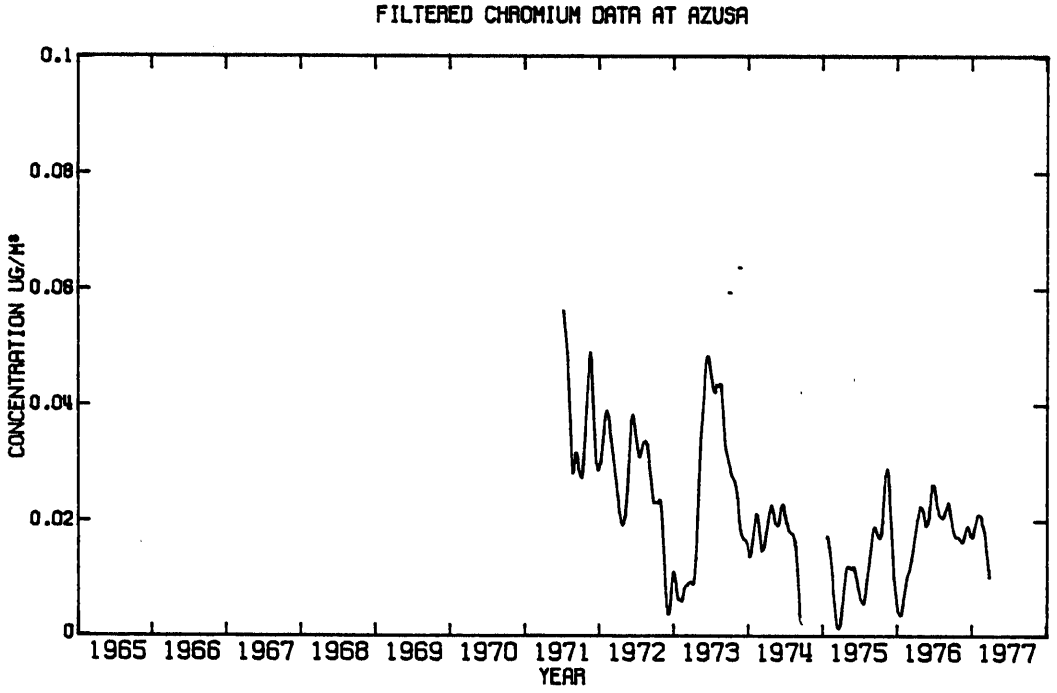



FIGURE A.3.2

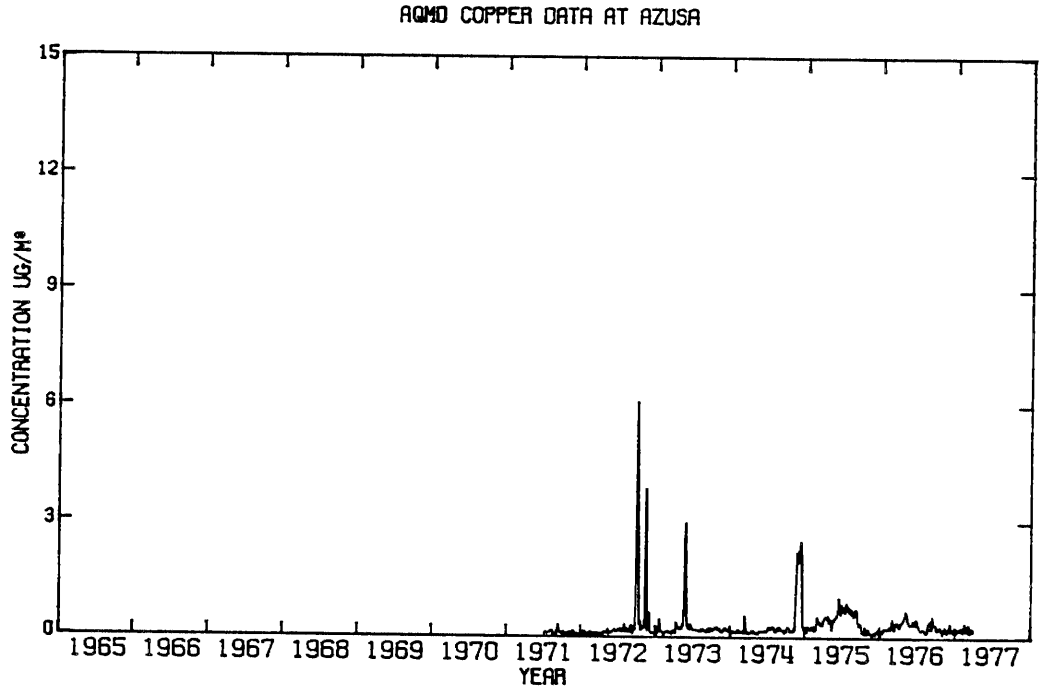



FIGURE A.3.3

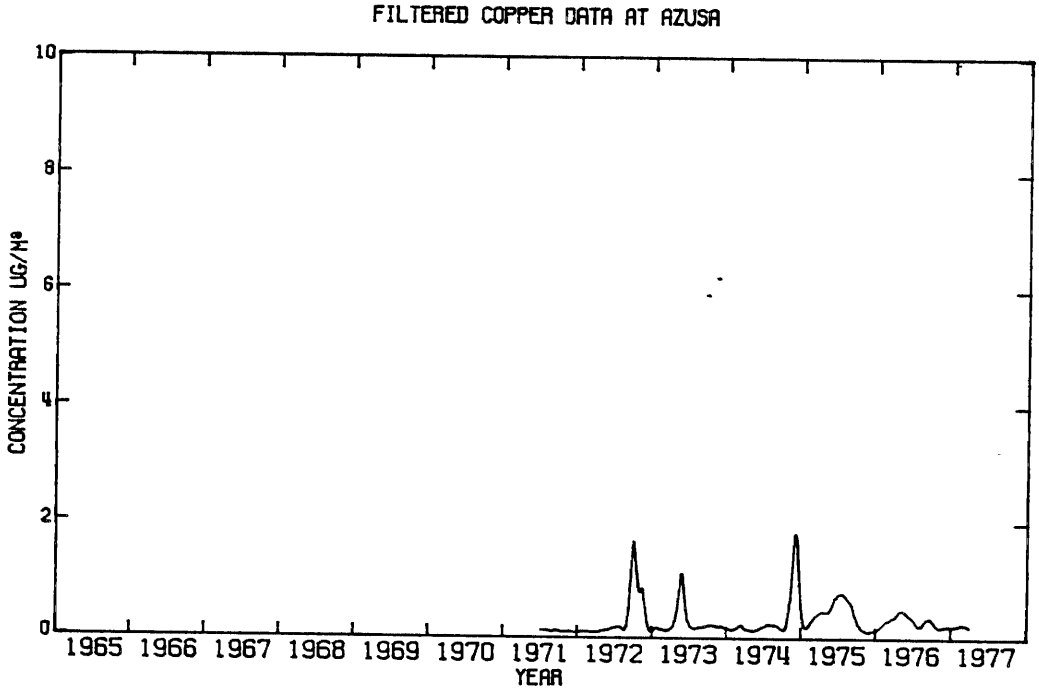



FIGURE A.3.4

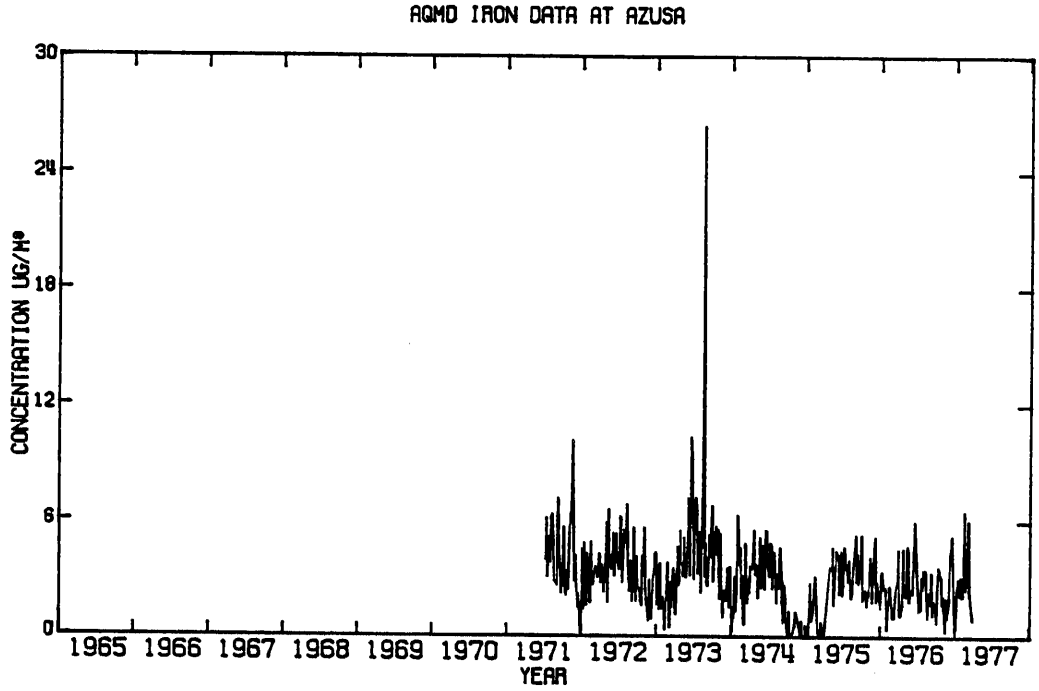



FIGURE A.3.5

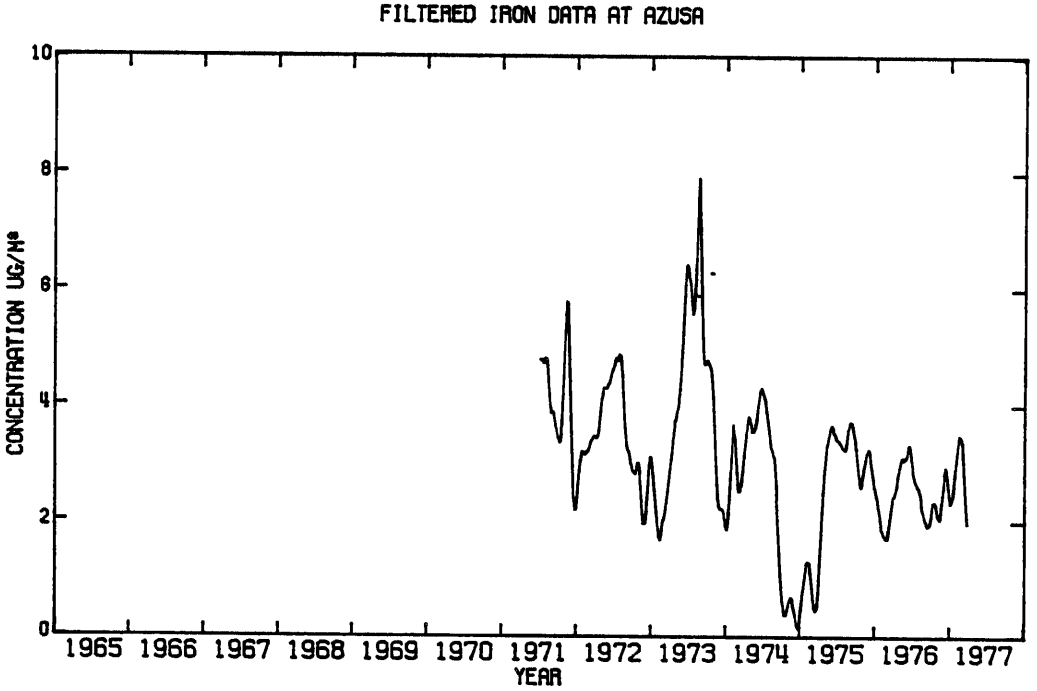



FIGURE A.3.6

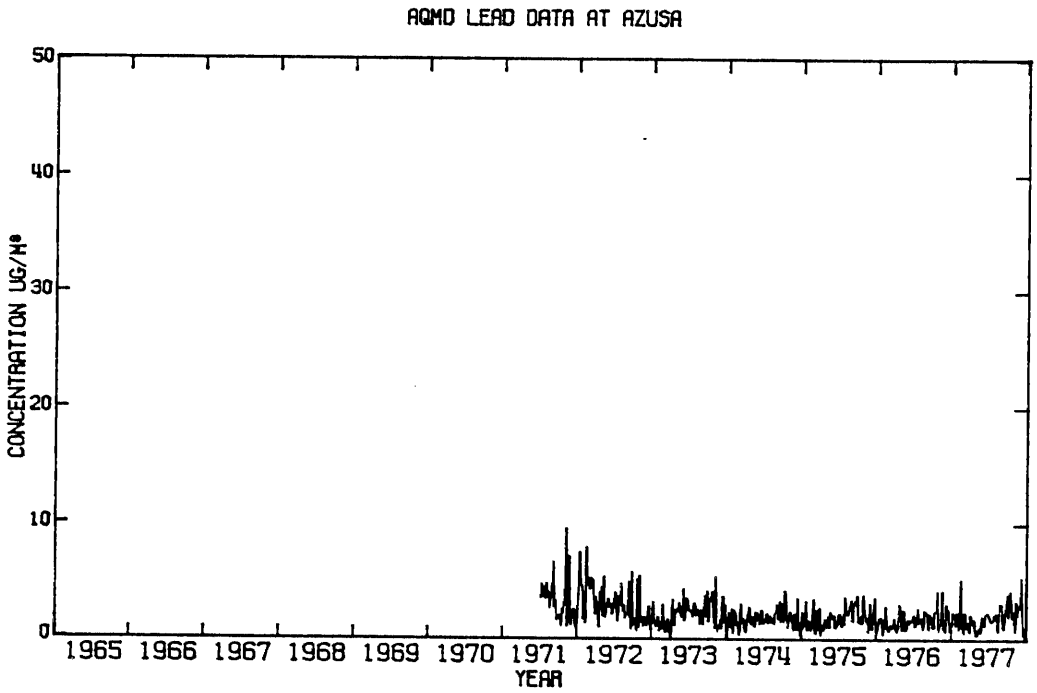



FIGURE A.3.7

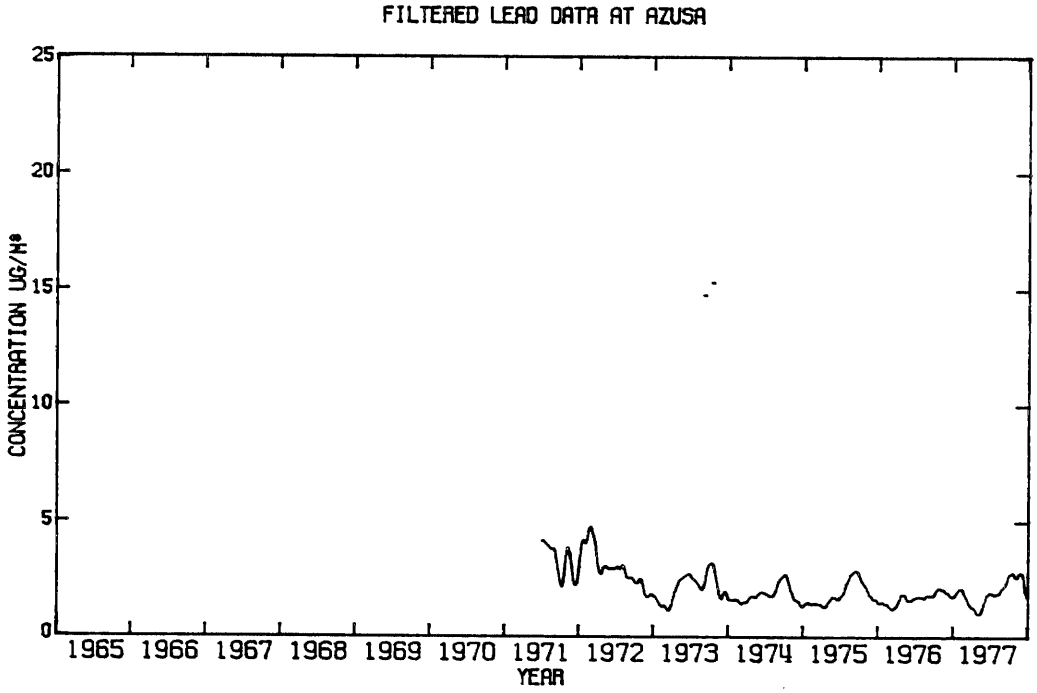



FIGURE A.3.8

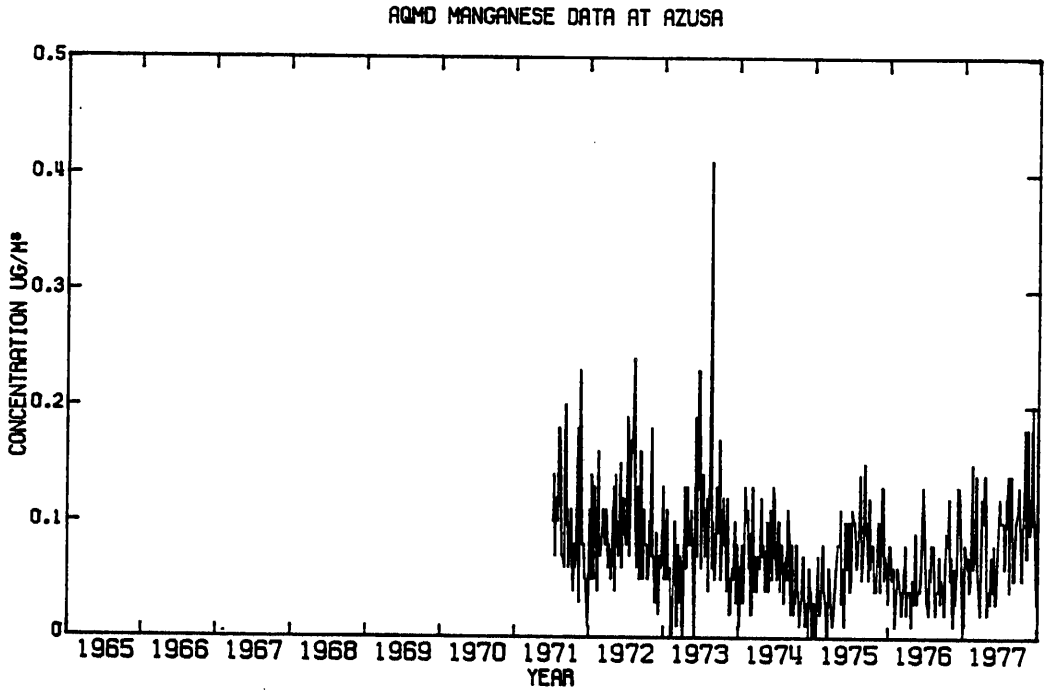



FIGURE A.3.9

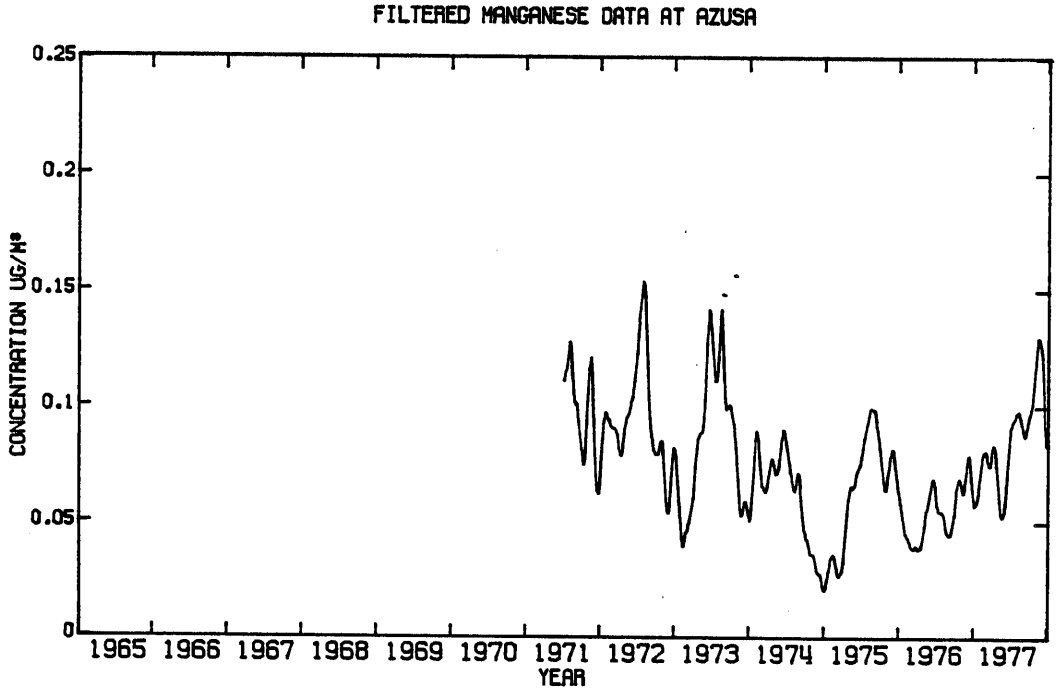



FIGURE A.3.10

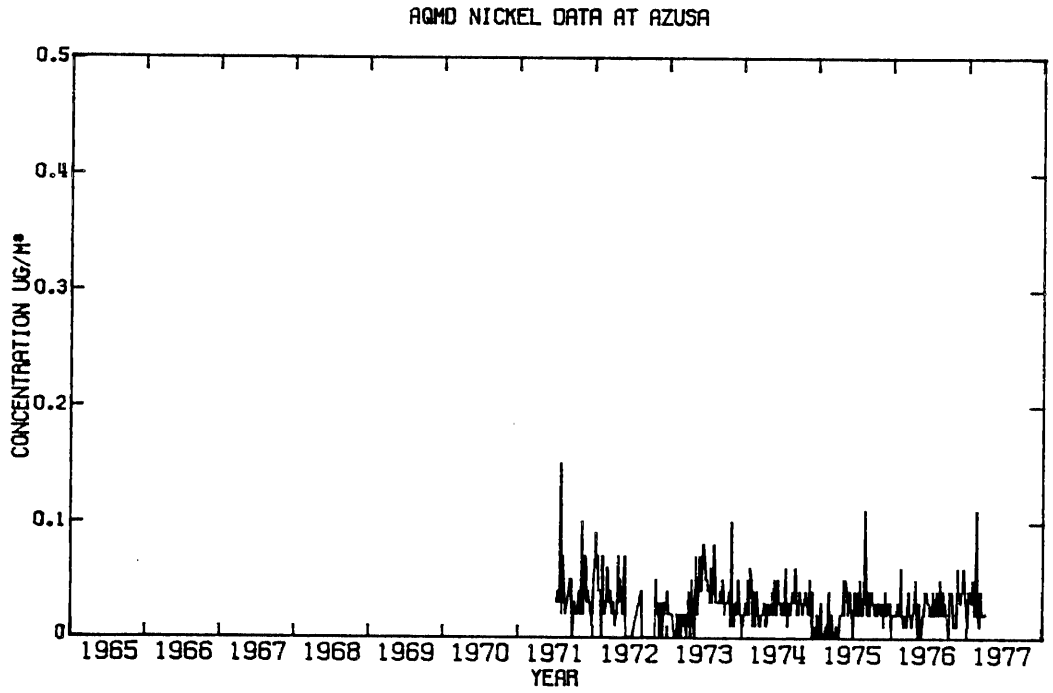



FIGURE A.3.11

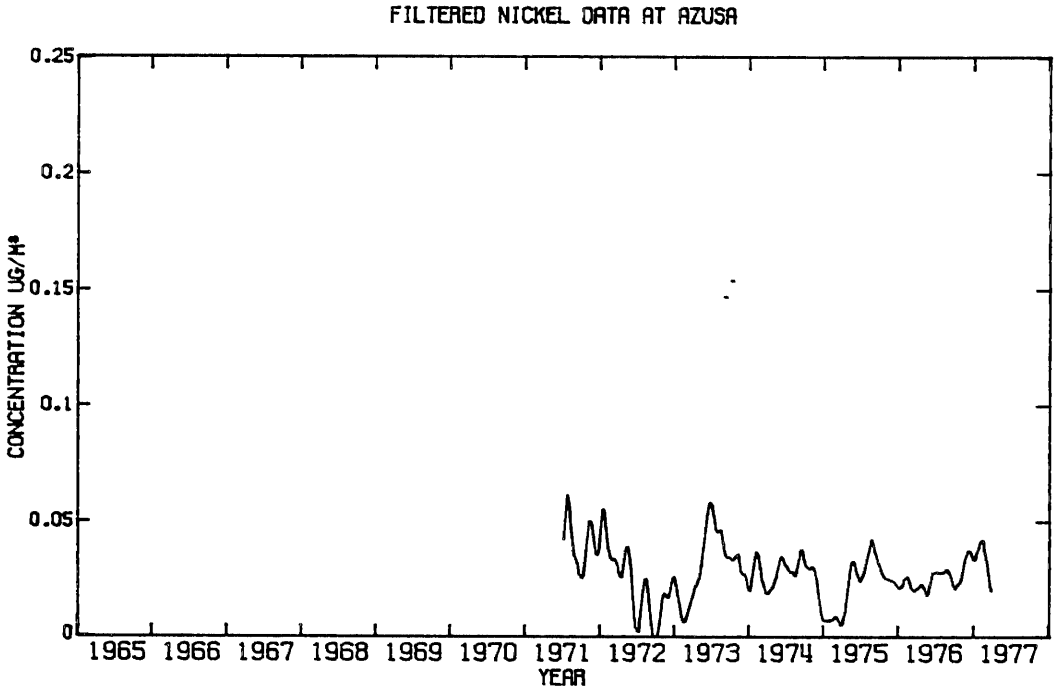



FIGURE A.3.12

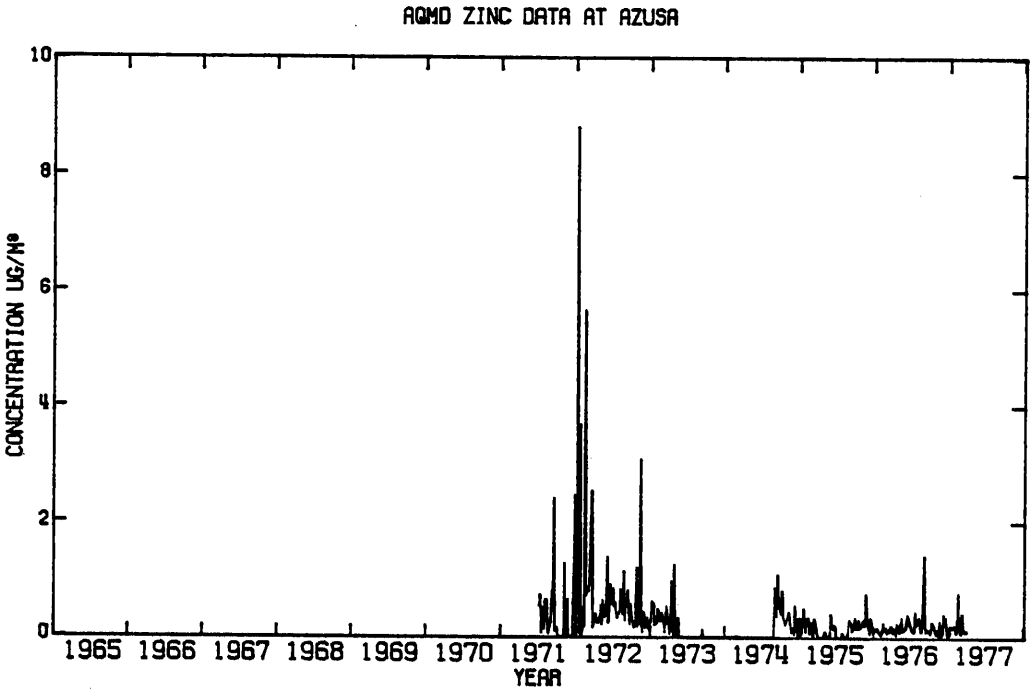



FIGURE A.3.13

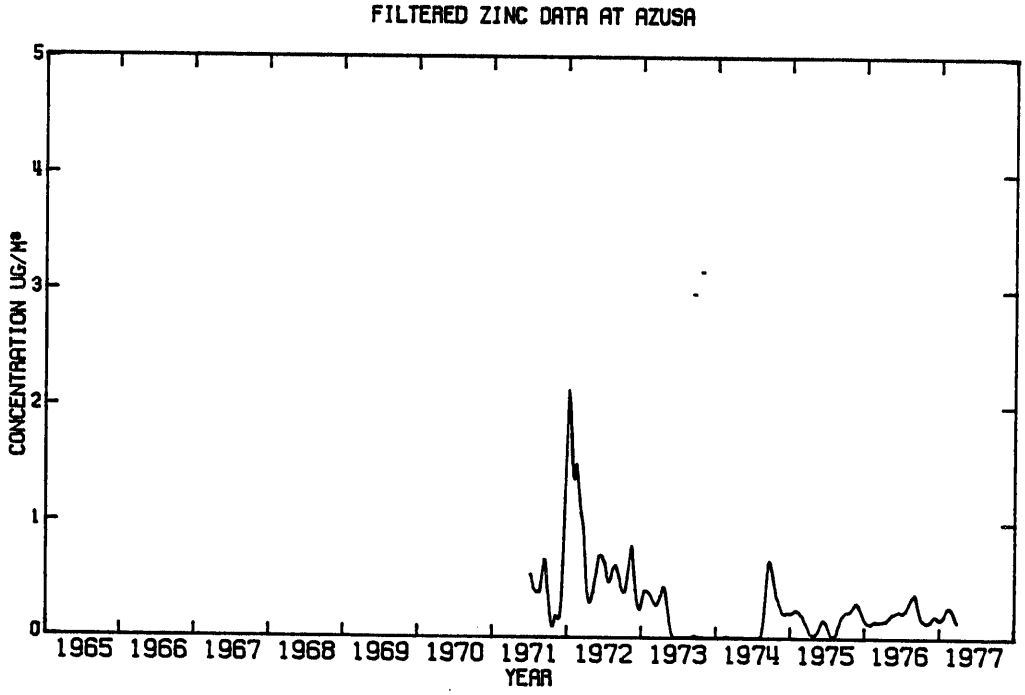



FIGURE A.3.14

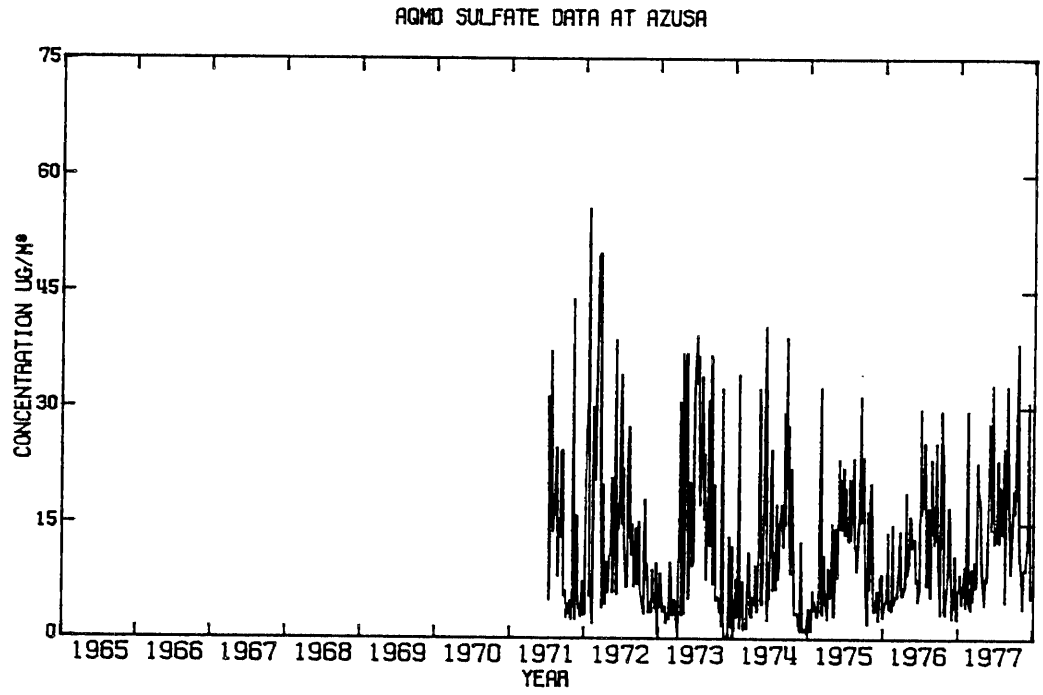



FIGURE A.3.15

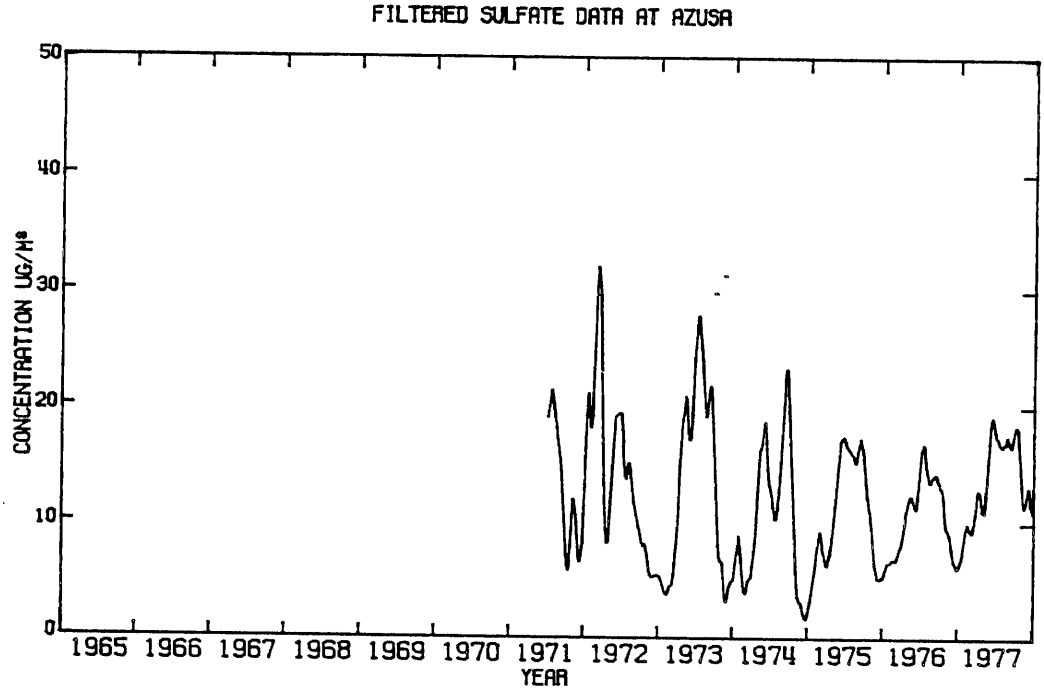



FIGURE A.3.16

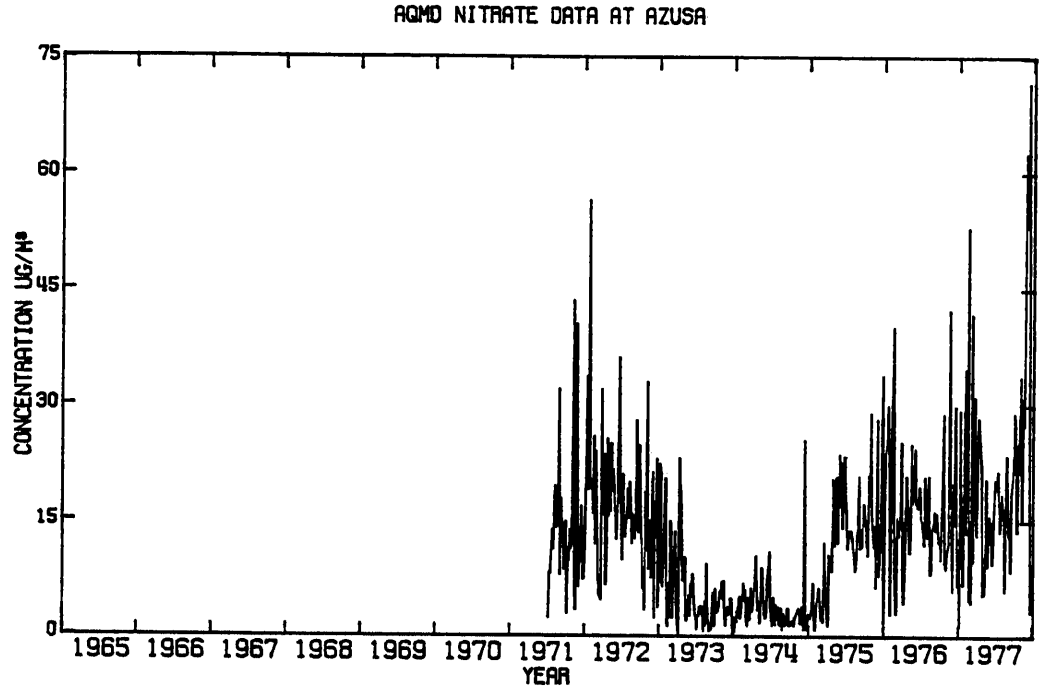



FIGURE A.3.17

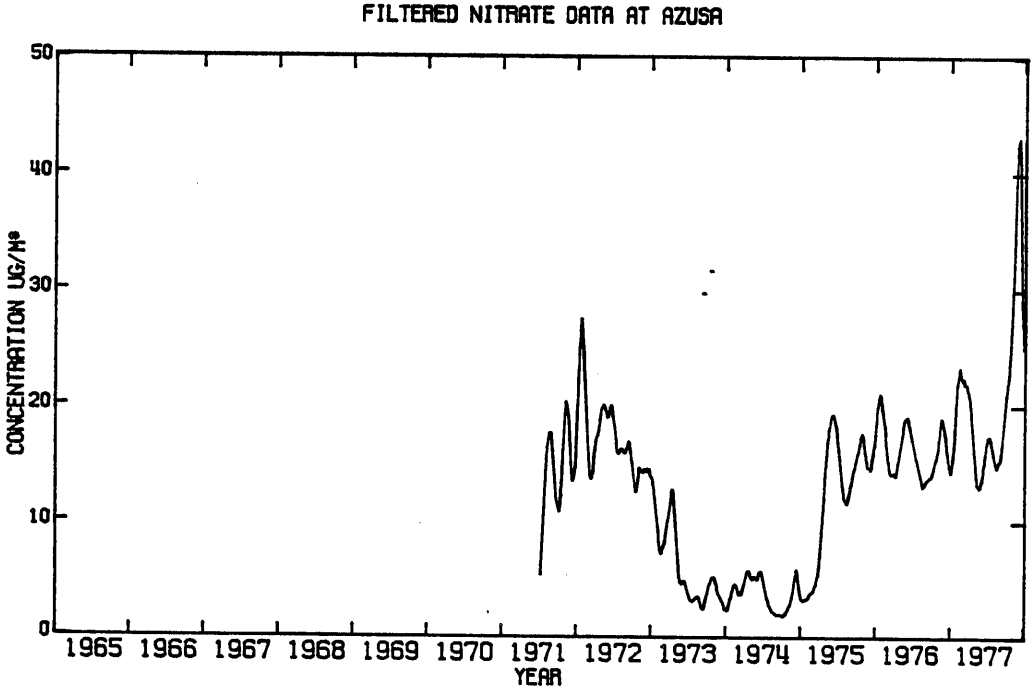



FIGURE A.3.18

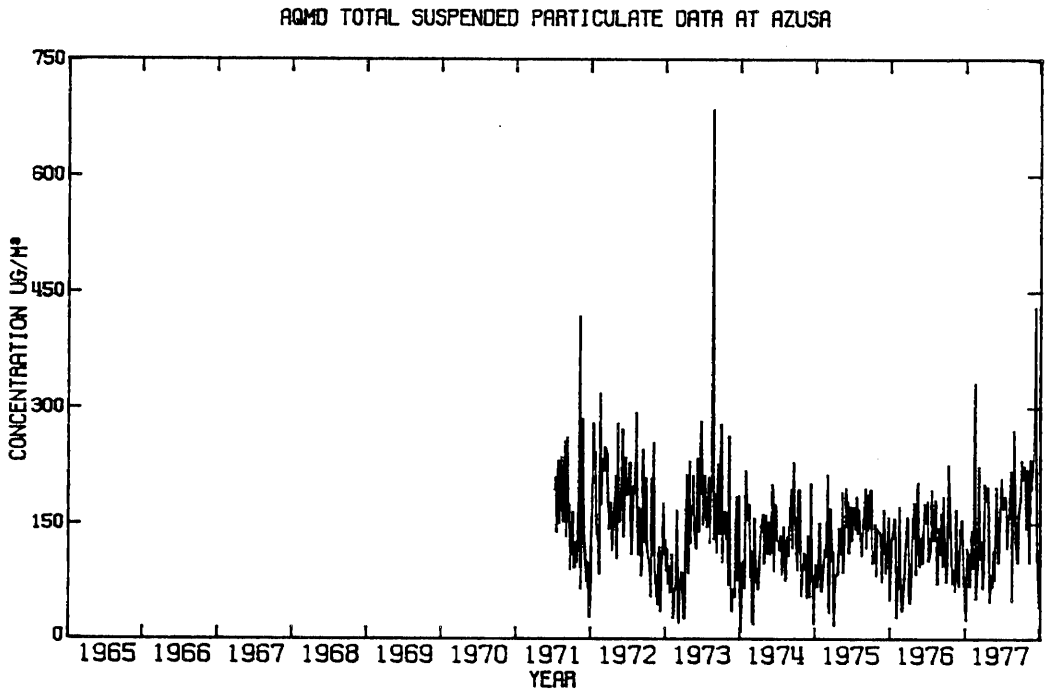



FIGURE A.3.19

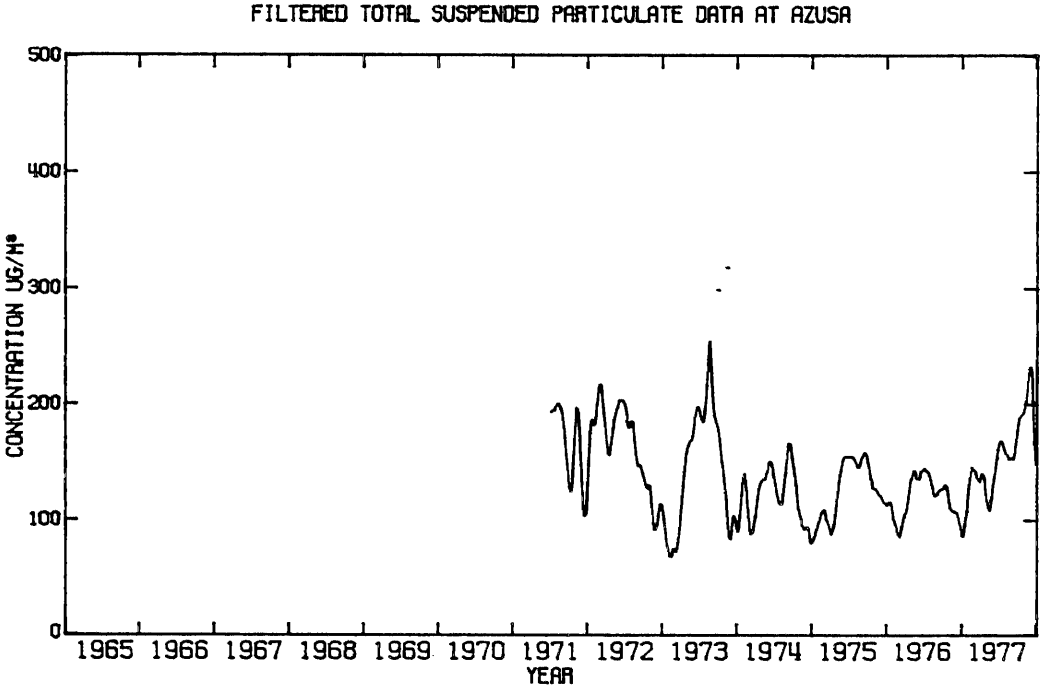



FIGURE A.3.20

## A.4 Monitoring Data at Downtown Los Angeles Site (SCAQMD)

TABLE A.4.1

Particulate Data Available at Downtown Los Angeles Monitoring Site (SCAQMD)

| Chemical Species | Figures[a] |
|---|---|
| Chromium | A.4.1 - A.4.2 |
| Copper | A.4.3 - A.4.4 |
| Iron | A.4.5 - A.4.6 |
| Lead | A.4.7 - A.4.8 |
| Manganese | A.4.9 - A.4.10 |
| Nickel | A.4.11 - A.4.12 |
| Zinc | A.4.13 - A.4.14 |
| Sulfates | A.4.15 - A.4.16 |
| Nitrates | A.4.17 - A.4.18 |
| Total Suspended Particulate | A.4.19 - A.4.20 |

a Odd numbered figures correspond to measured data and even numbered ones to filtered results.

TABLE A.4.2

Summary of Particulate Air Quality Statistics
at Downtown Los Angeles Monitoring Site (SCAQMD)
(Aug 1965 - Dec 1977)

| Chemical Species | Number of Samples | Statistics | | |
|---|---|---|---|---|
| | | Mean | Maximum | Minimum |
| | | (Micrograms $m^{-3}$) | | |
| Chromium | 714 | 0.018 | 0.07 | 0.00 |
| Copper | 758 | 0.189 | 9.10 | 0.00 |
| Iron | 747 | 2.18 | 15.73 | 0.00 |
| Lead | 788 | 3.80 | 24.70 | 0.00 |
| Manganese | 788 | 0.046 | 0.26 | 0.00 |
| Nickel | 757 | 0.033 | 0.24 | 0.00 |
| Zinc | 719 | 0.648 | 6.11 | 0.00 |
| Sulfates | 795 | 13.0 | 72.0 | 0.00 |
| Nitrates | 795 | 11.2 | 68.9 | 0.10 |
| TSP | 798 | 139.9 | 412.0 | 24.0 |

Note: All samples are 24 hour averages

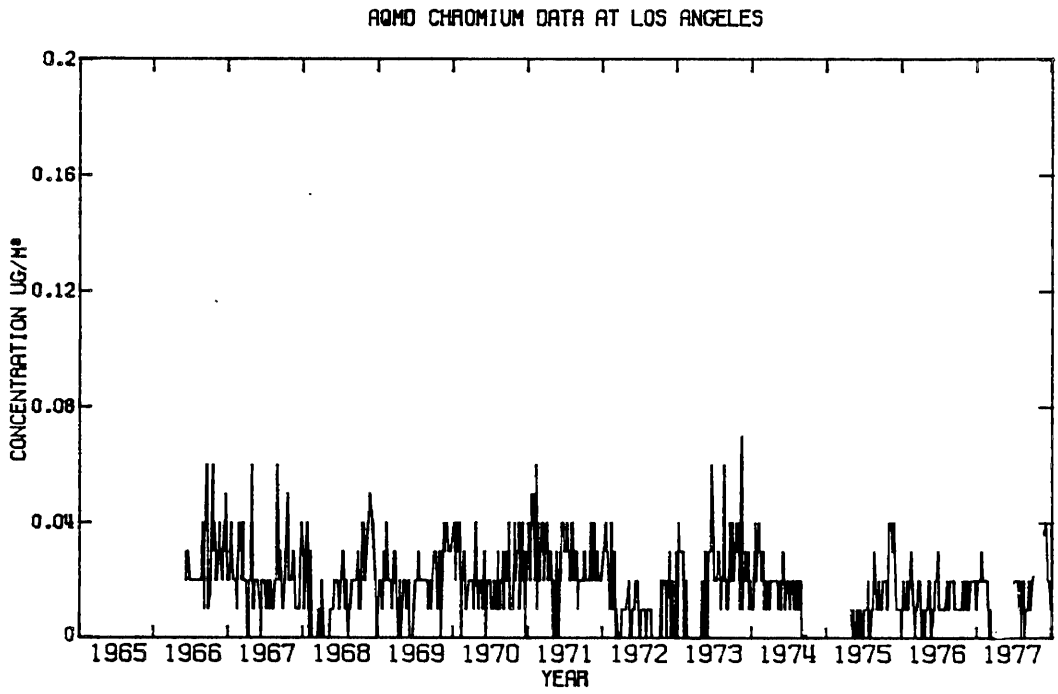



FIGURE A.4.1

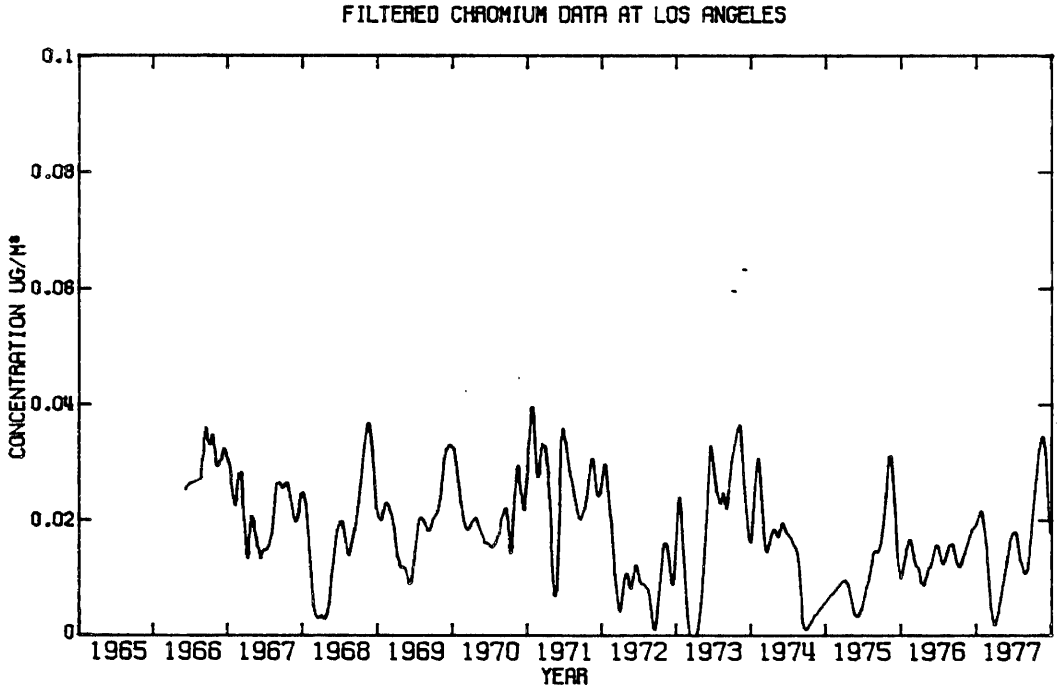



FIGURE A.4.2

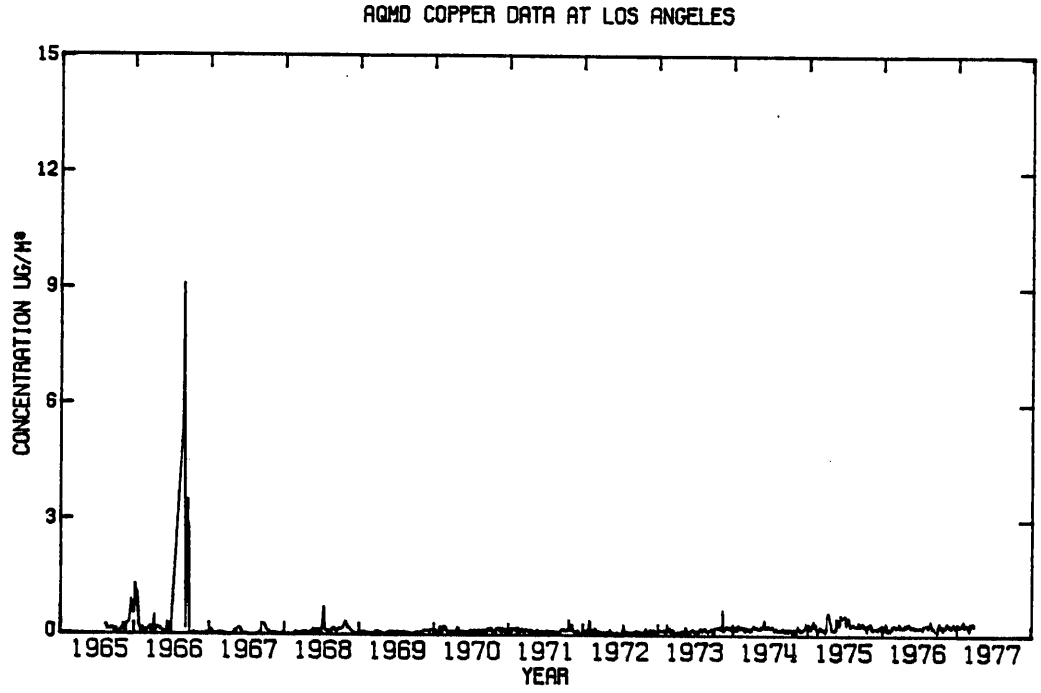



FIGURE A.4.3

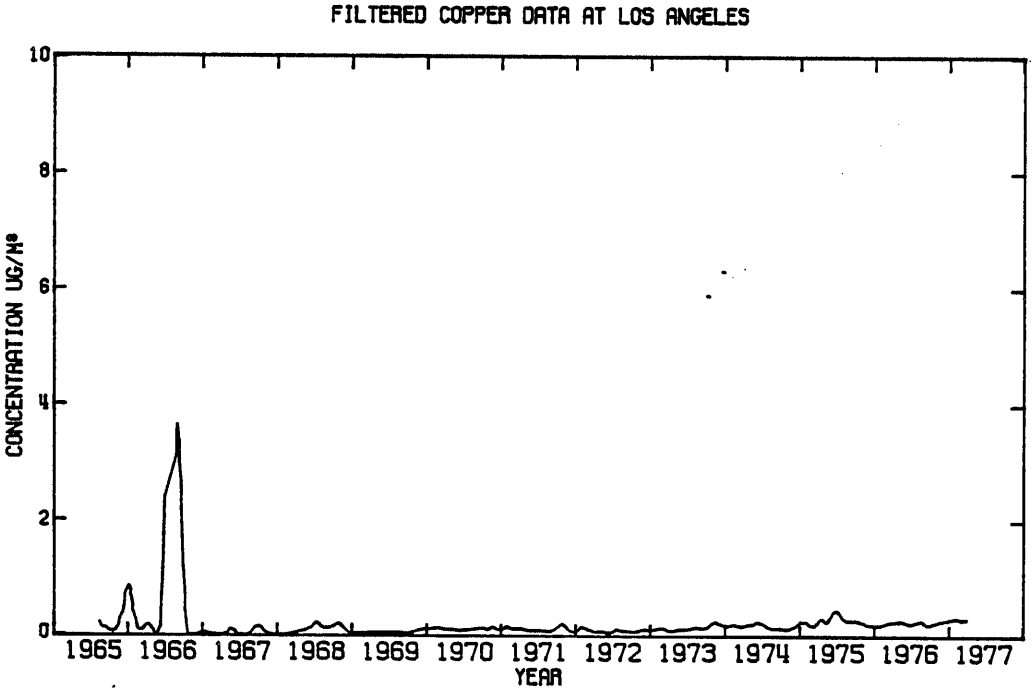



FIGURE A.4.4

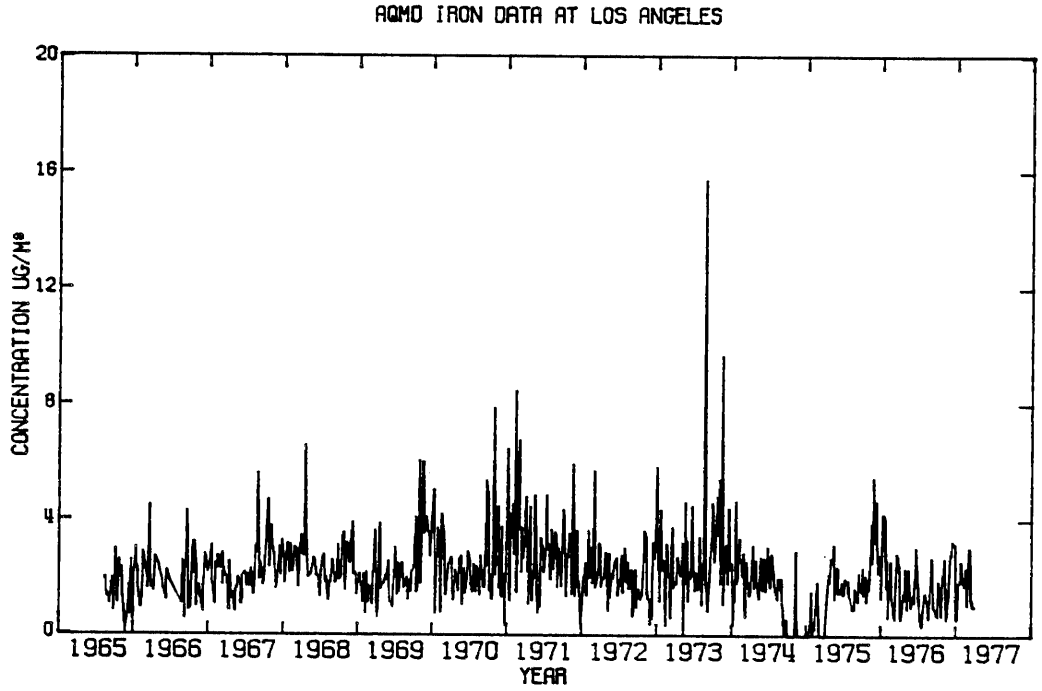



FIGURE A.4.5

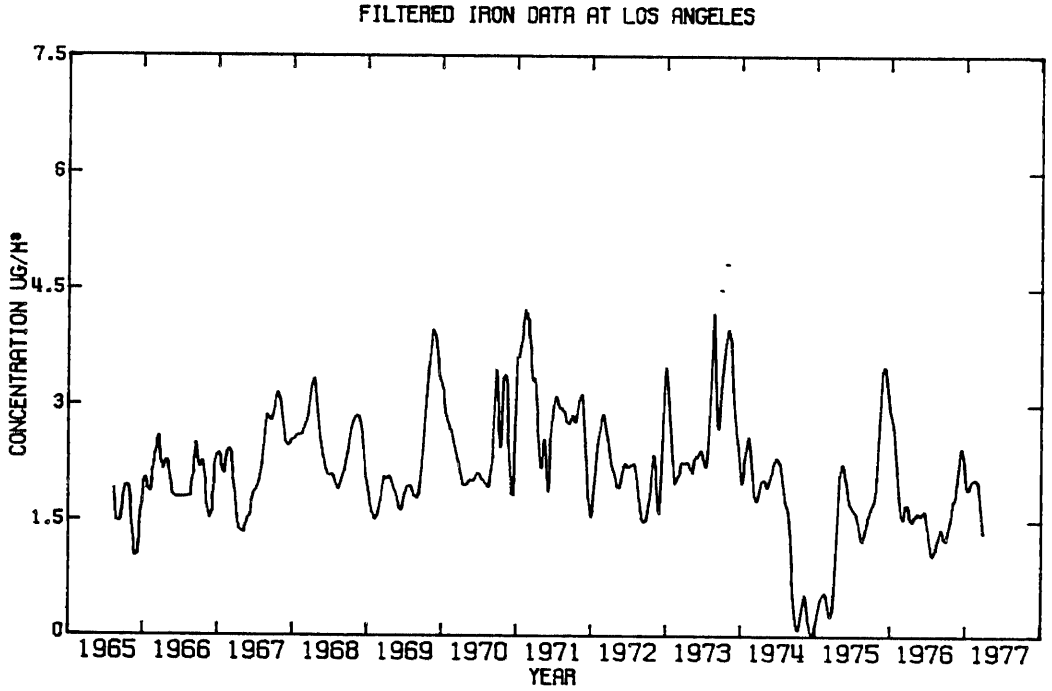



FIGURE A.4.6

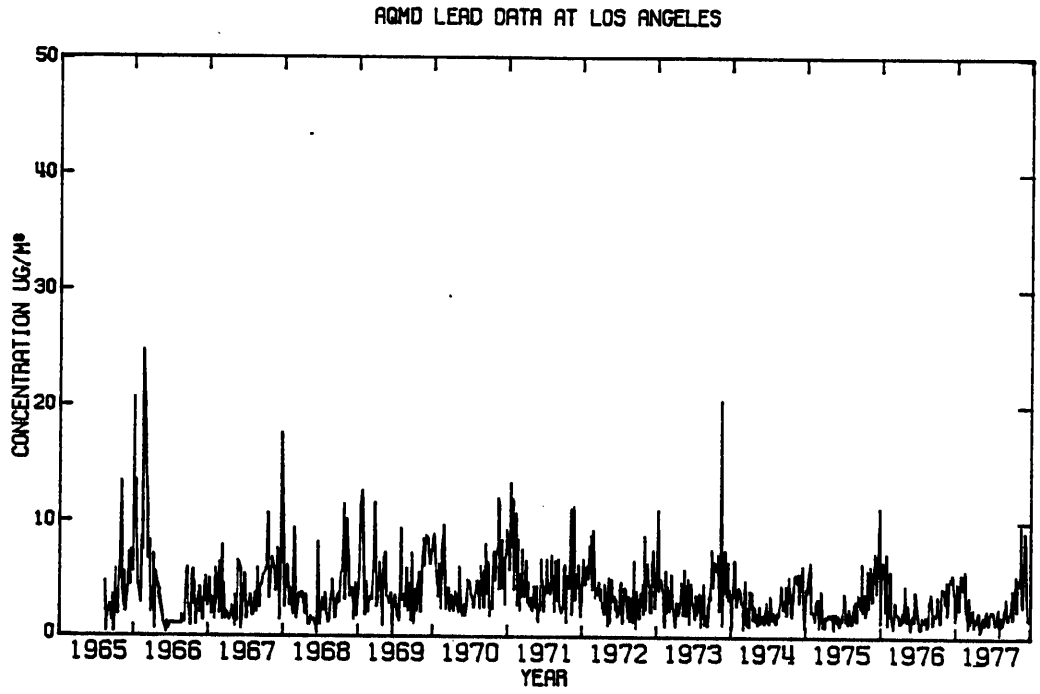



FIGURE A.4.7

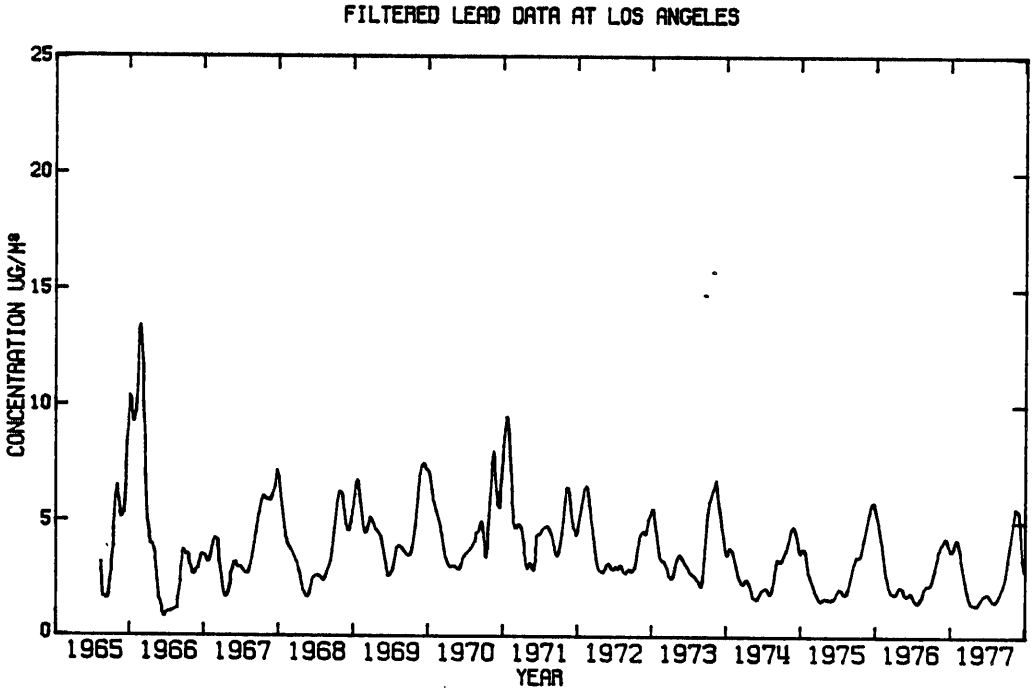



FIGURE A.4.8

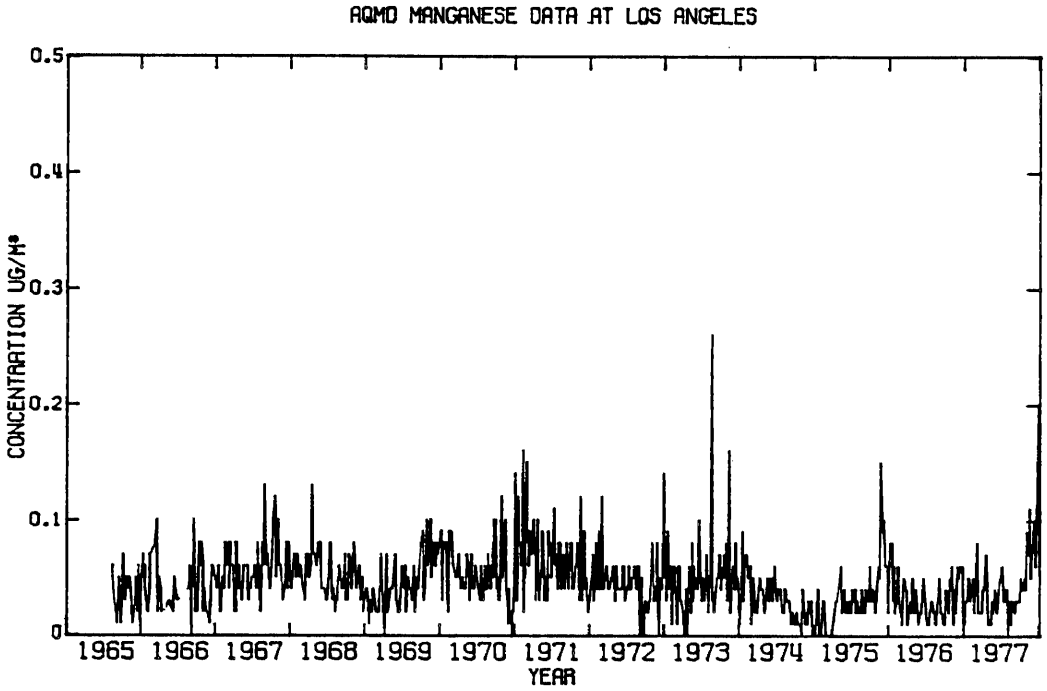



FIGURE A.4.9

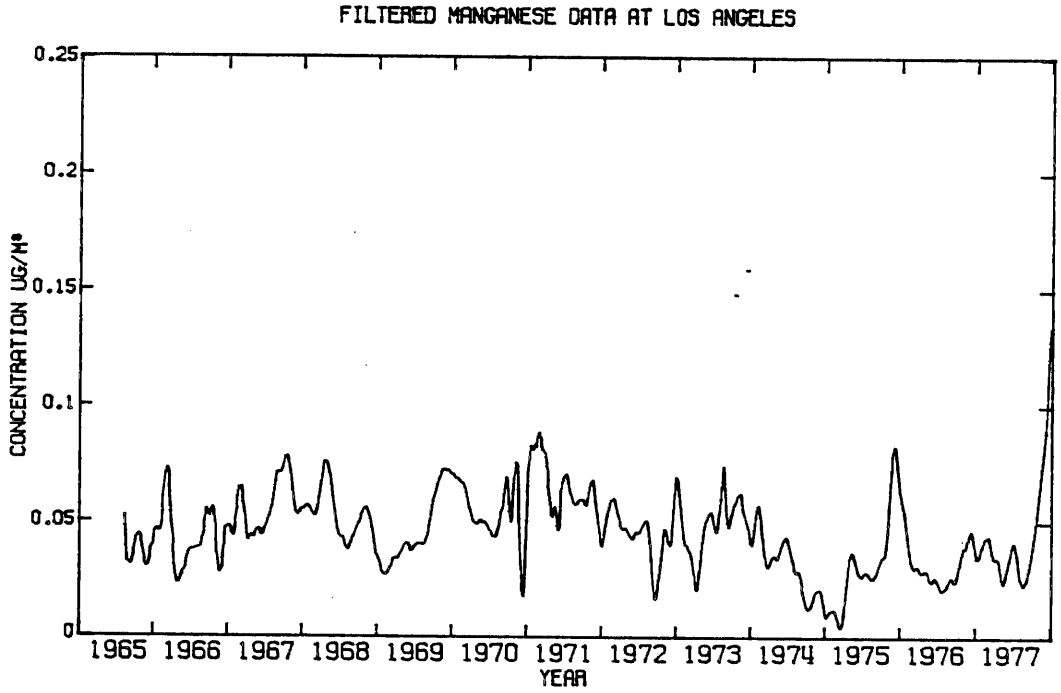



FIGURE A.4.10

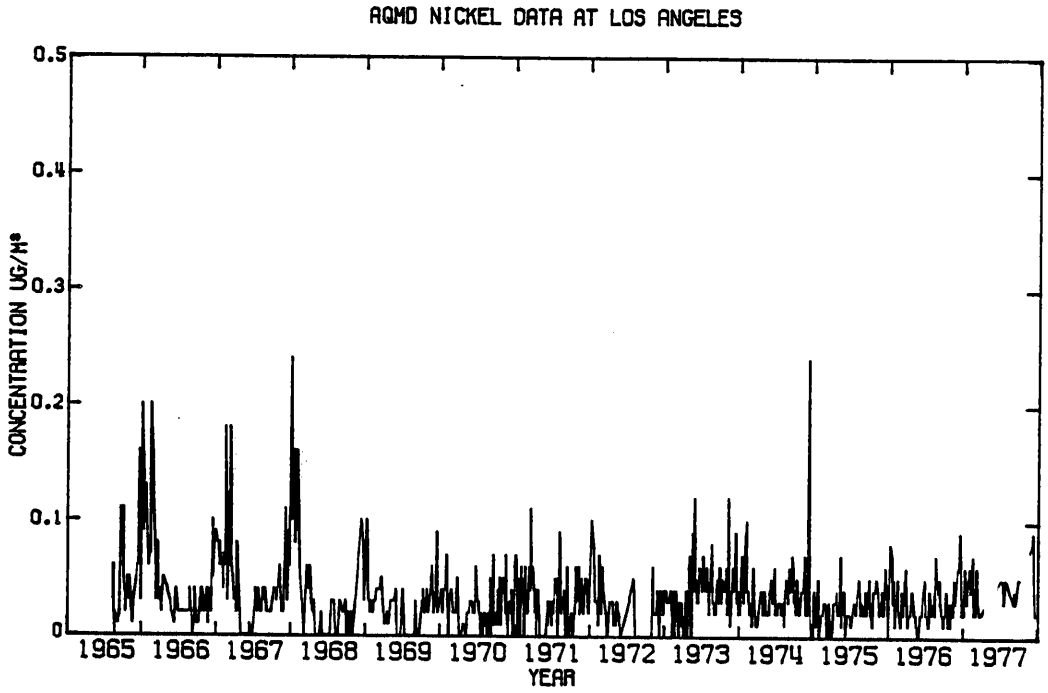



FIGURE A.4.11

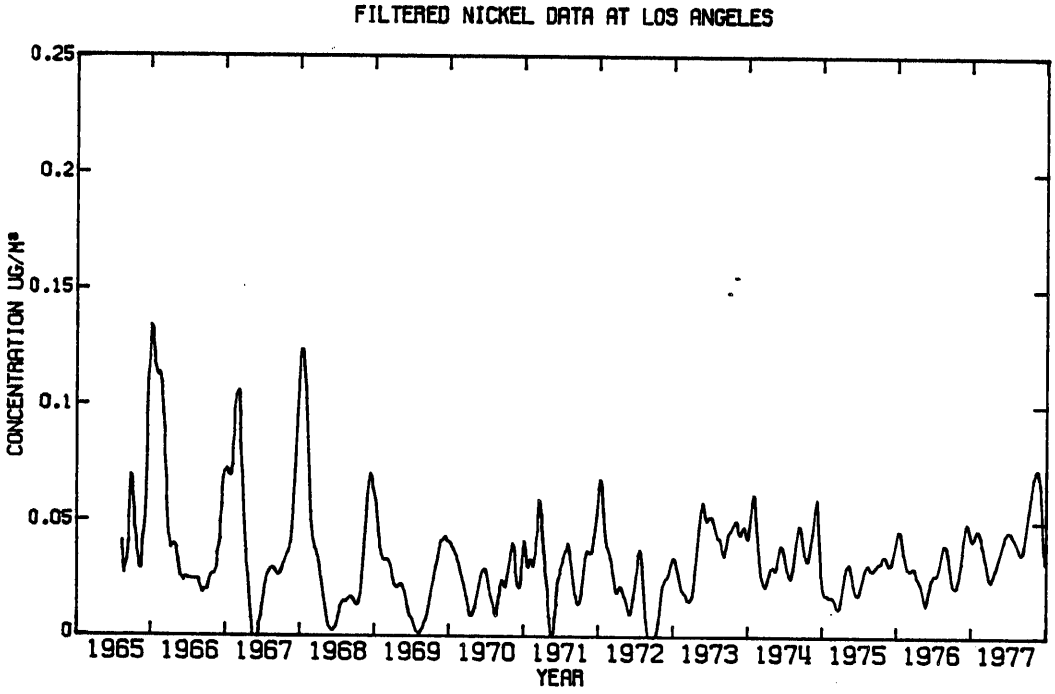



FIGURE A.4.12

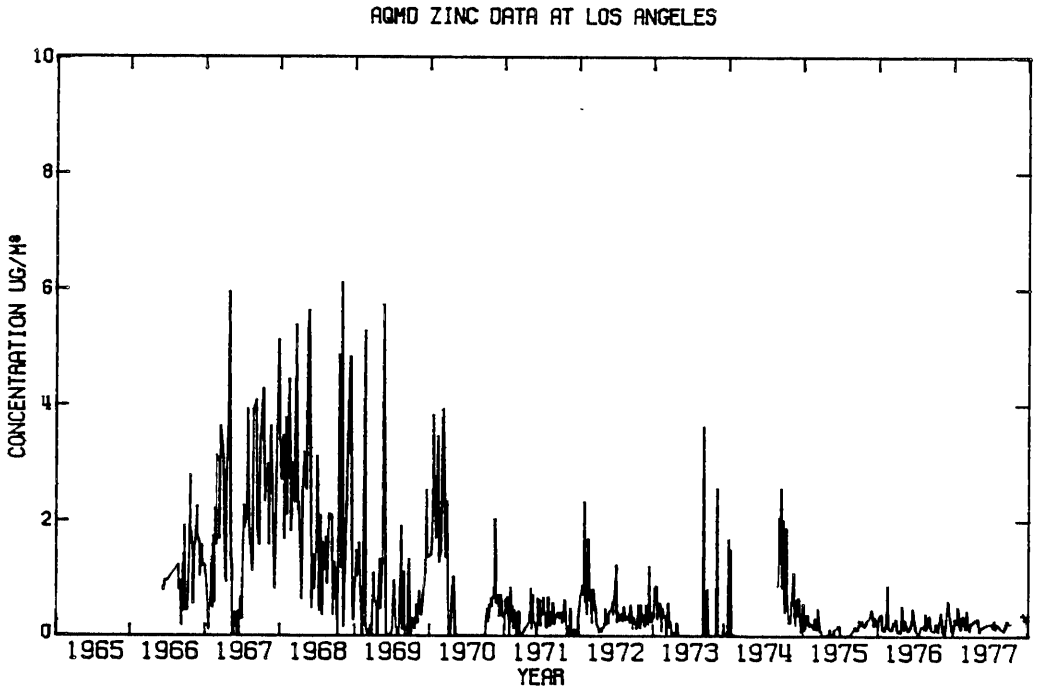



FIGURE A.4.13

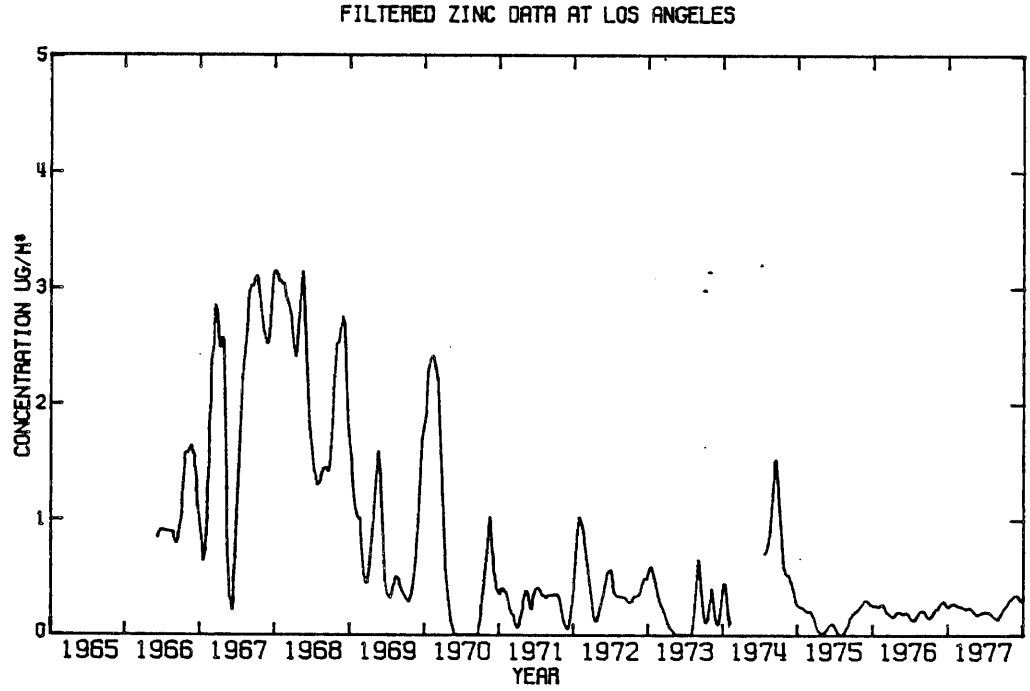



FIGURE A.4.14

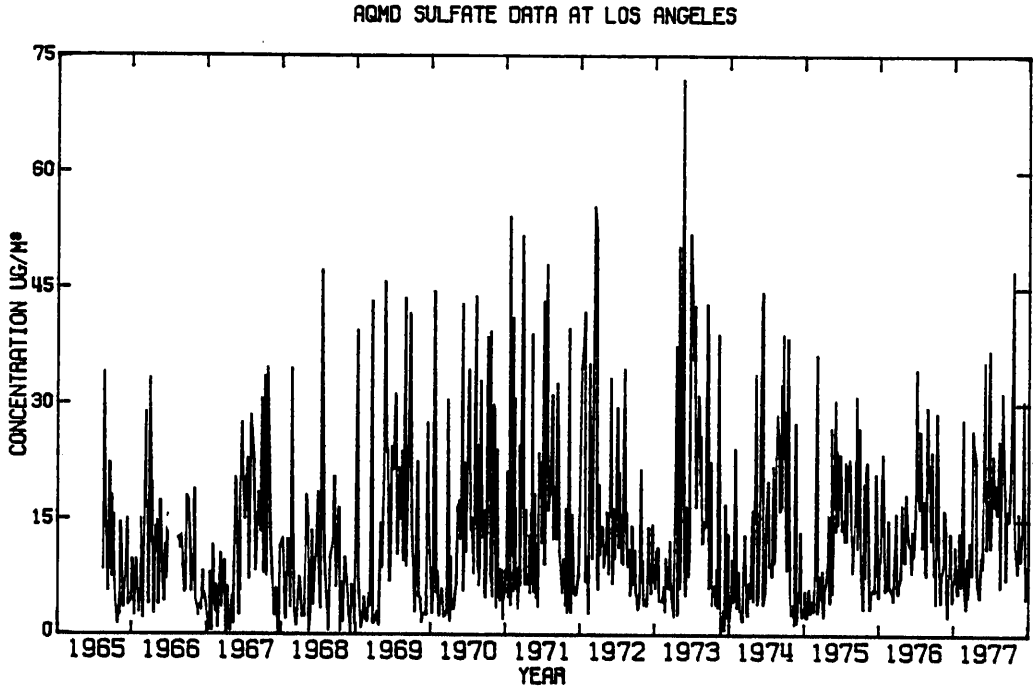



FIGURE A.4.15

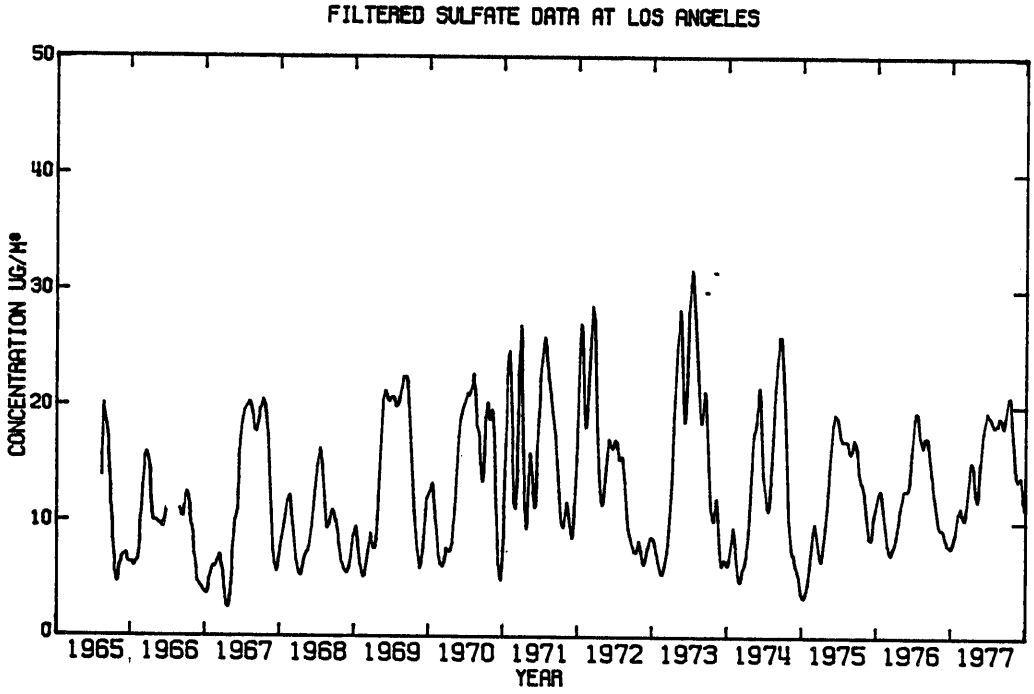



FIGURE A.4.16

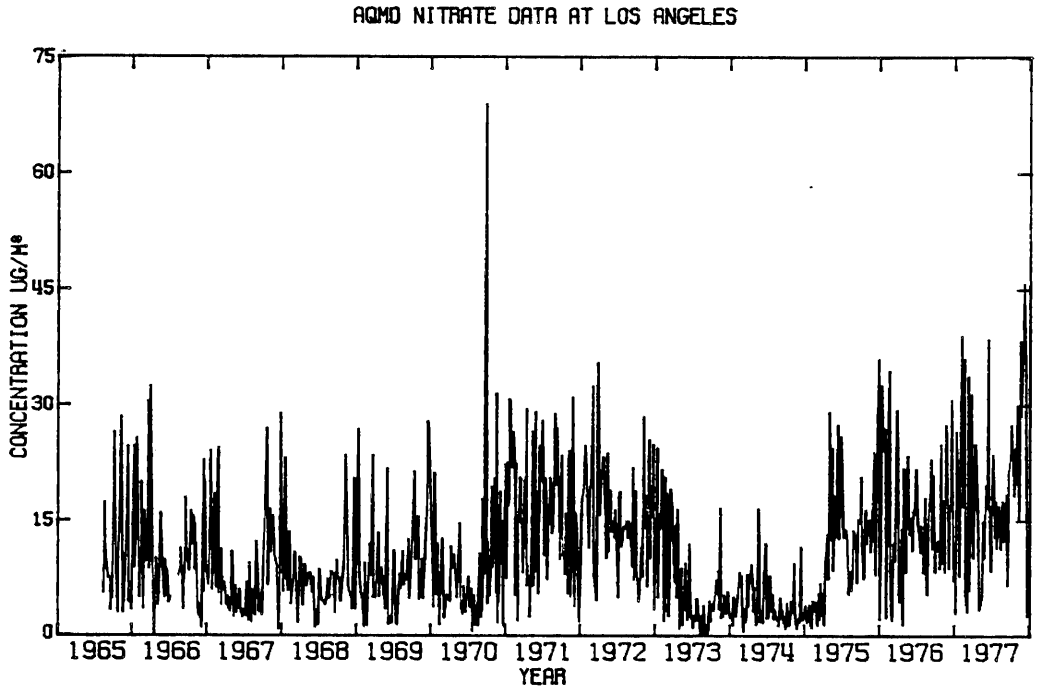



FIGURE A.4.17

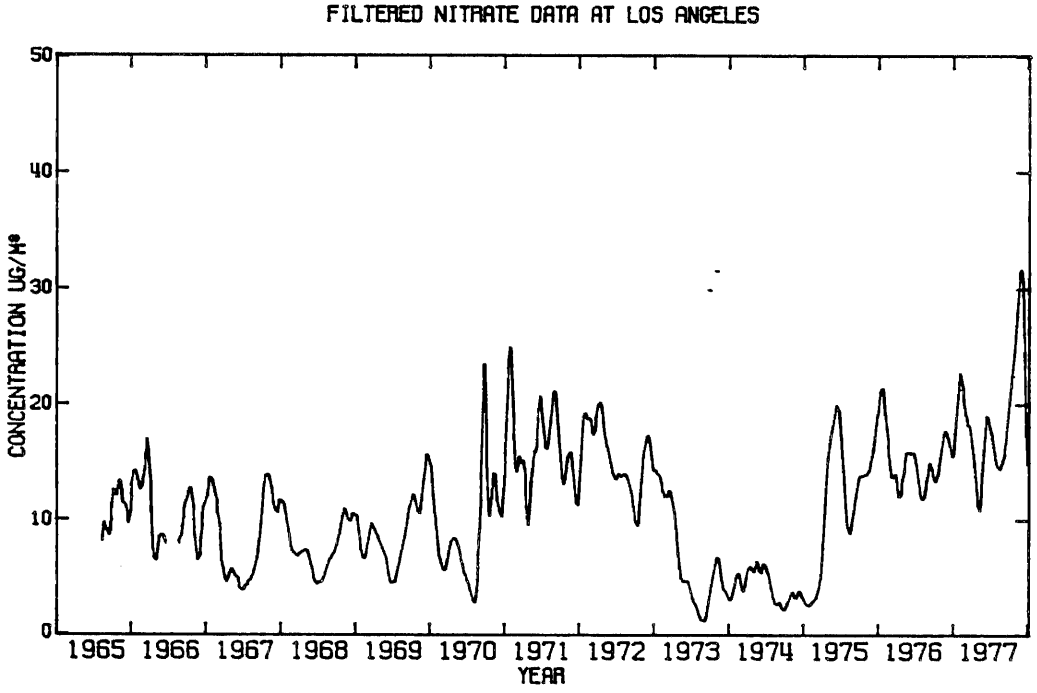



FIGURE A.4.18

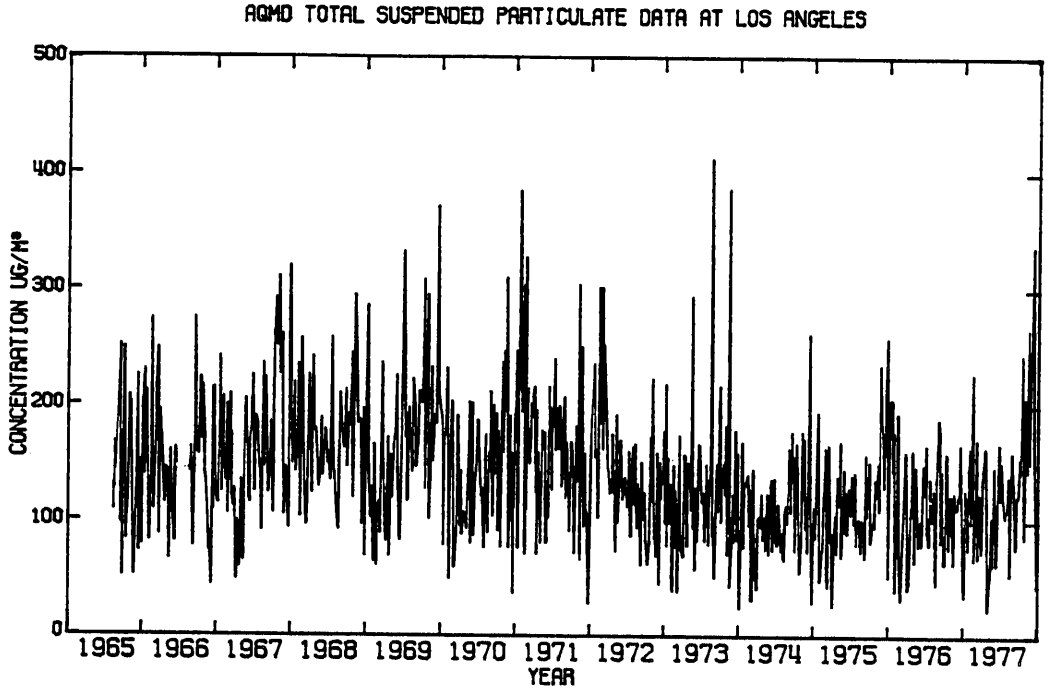



FIGURE A.4.19

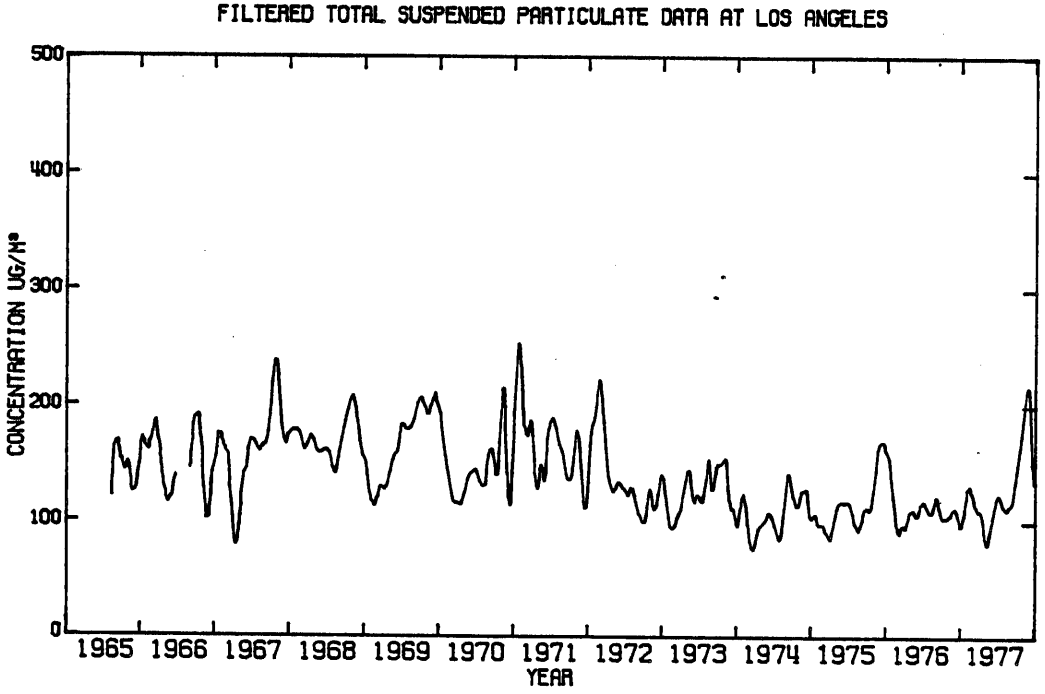



FIGURE A.4.20

## A.5 Monitoring Data at Lennox Site (SCAQMD)

TABLE A.5.1

Particulate Data Available at Lennox Monitoring Site (SCAQMD)

| Chemical Species | Figures[a] |
|---|---|
| Chromium | A.5.1 - A.5.2 |
| Copper | A.5.3 - A.5.4 |
| Iron | A.5.5 - A.5.6 |
| Lead | A.5.7 - A.5.8 |
| Manganese | A.5.9 - A.5.10 |
| Nickel | A.5.11 - A.5.12 |
| Zinc | A.5.13 - A.5.14 |
| Sulfates | A.5.15 - A.5.16 |
| Nitrates | A.5.17 - A.5.18 |
| Total Suspended Particulate | A.5.19 - A.5.20 |

a Odd numbered figures correspond to measured data and even numbered ones to filtered results.

TABLE A.5.2

Summary of Particulate Air Quality Statistics
at Lennox Monitoring Site (SCAQMD)
(Aug 1965 - Dec 1977)

| Chemical Species | Number of Samples | Statistics | | |
|---|---|---|---|---|
| | | Mean | Maximum | Minimum |
| | | (Micrograms $m^{-3}$) | | |
| Chromium | 706 | 0.014 | 0.06 | 0.00 |
| Copper | 764 | 0.31 | 13.67 | 0.00 |
| Iron | 747 | 2.05 | 10.10 | 0.00 |
| Lead | 781 | 5.58 | 37.2 | 0.29 |
| Manganese | 787 | 0.041 | 0.22 | 0.00 |
| Nickel | 754 | 0.043 | 0.34 | 0.00 |
| Zinc | 715 | 0.59 | 7.91 | 0.00 |
| Sulfates | 797 | 12.49 | 54.9 | 0.00 |
| Nitrates | 798 | 7.54 | 73.0 | 0.00 |
| TSP | 796 | 136.03 | 344.0 | 19.00 |

Note: All samples are 24 hour averages

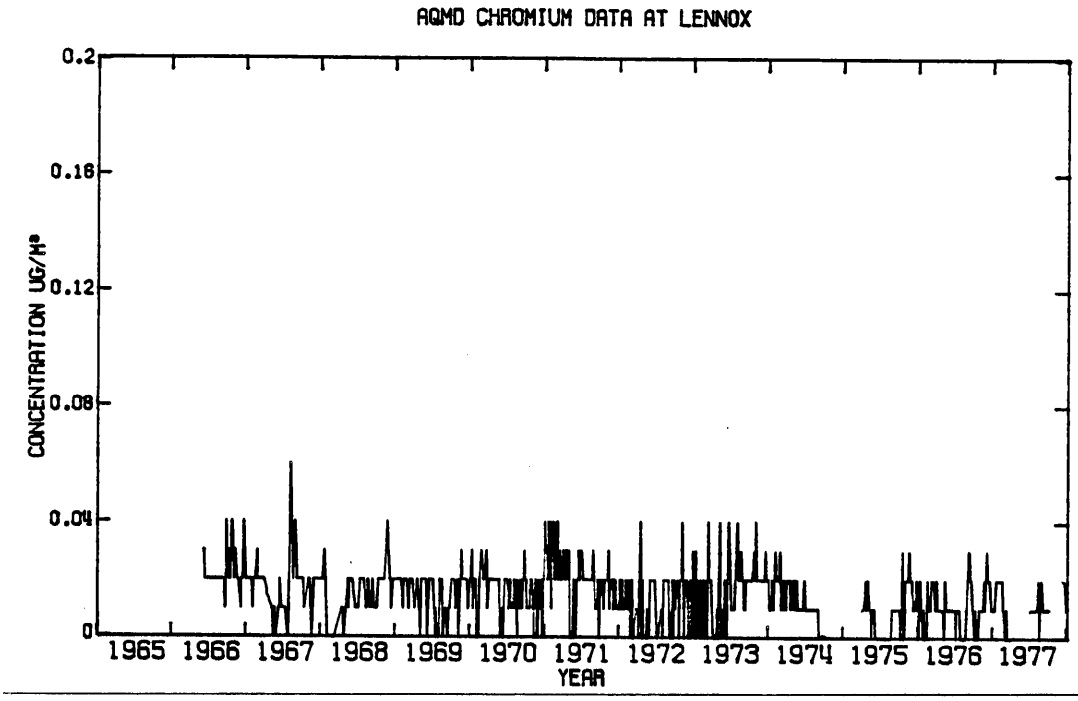



FIGURE A.5.1

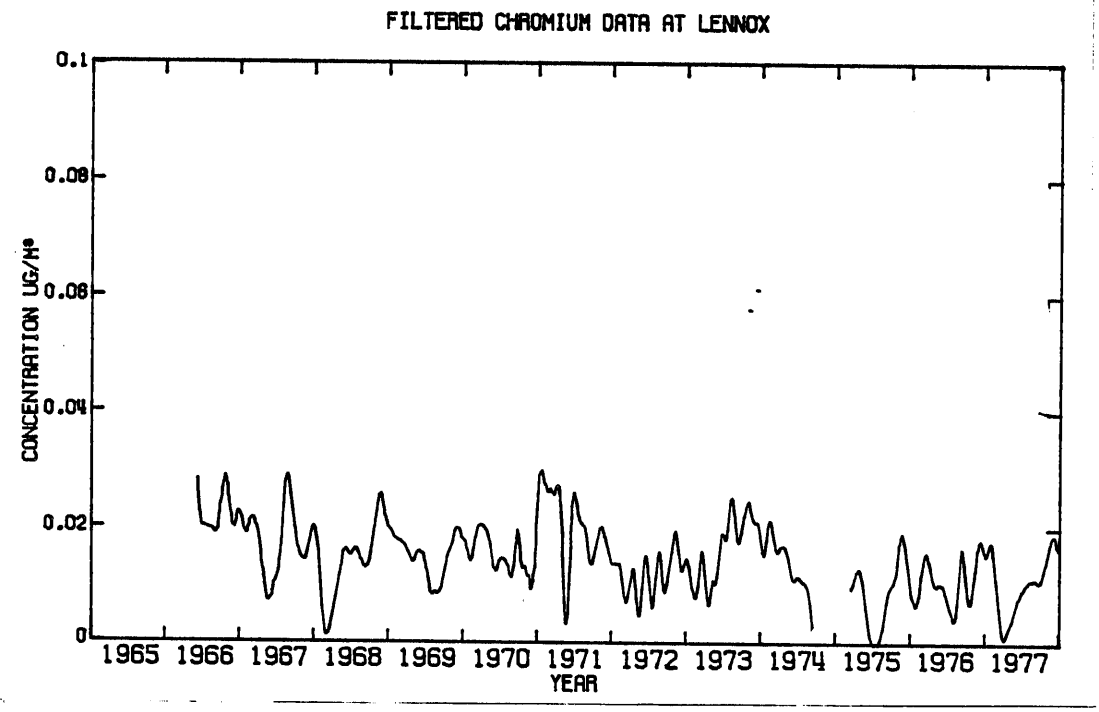



FIGURE A.5.2

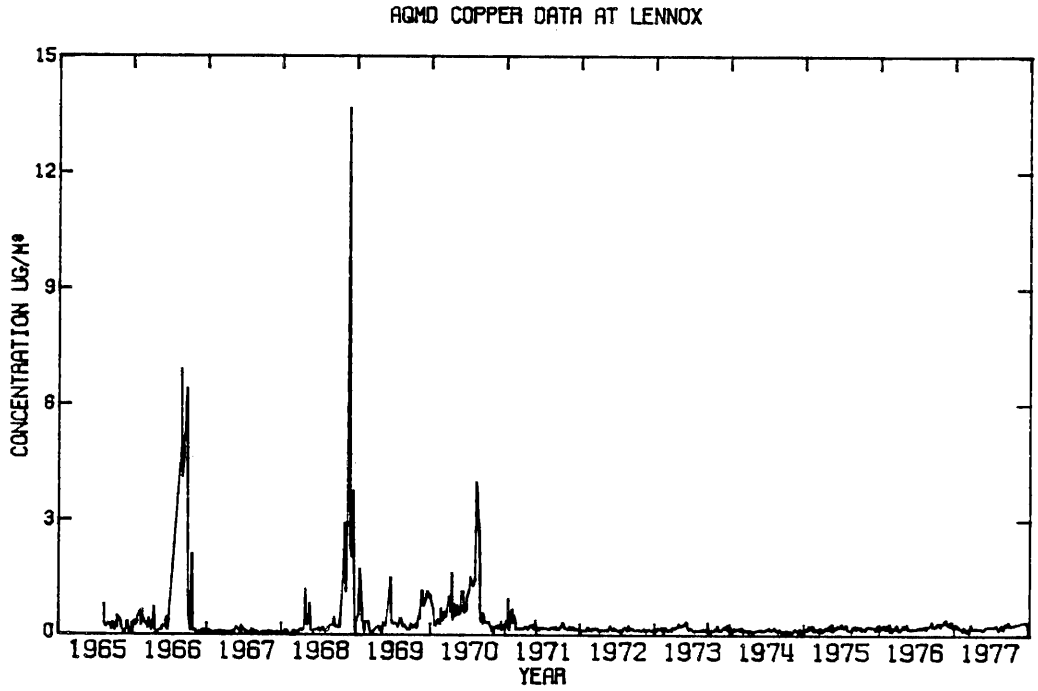



FIGURE A.5.3

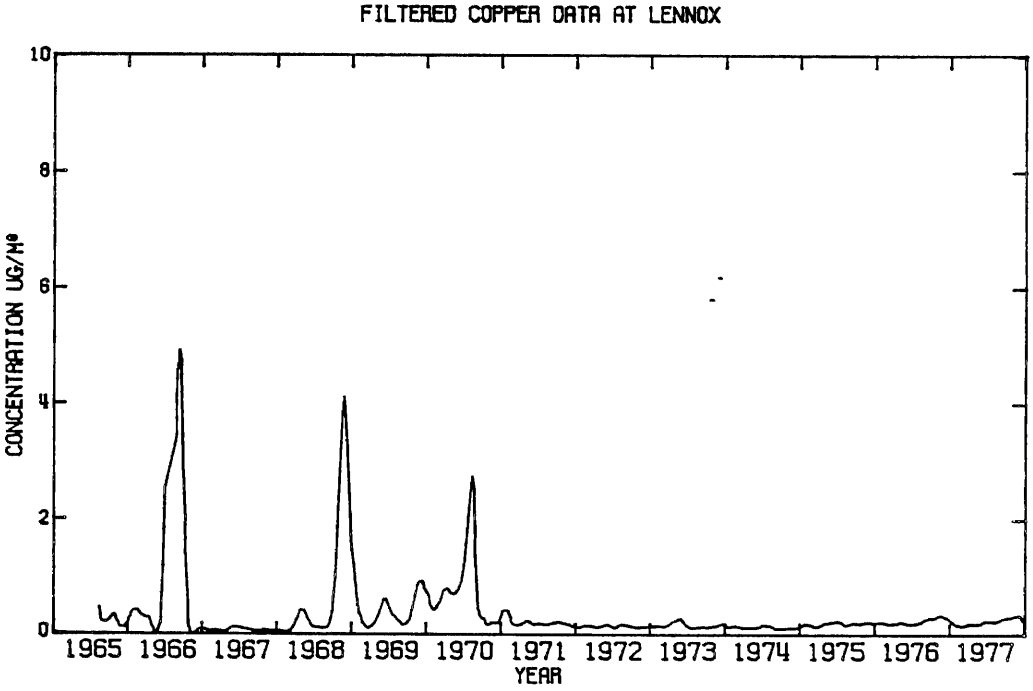



FIGURE A.5.4

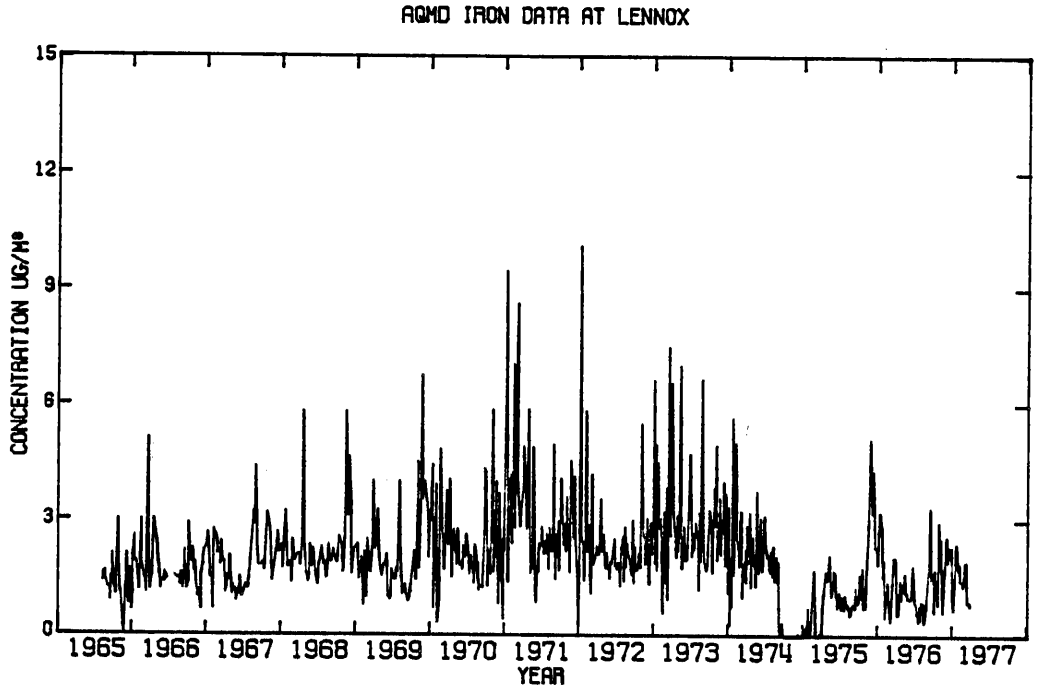



FIGURE A.5.5

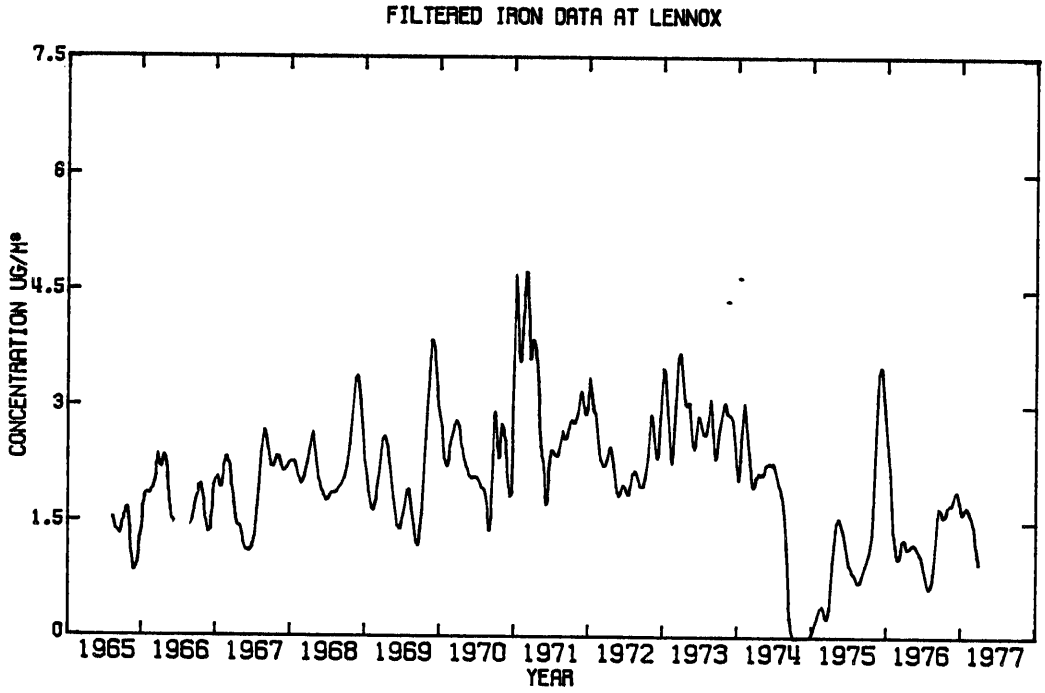



FIGURE A.5.6

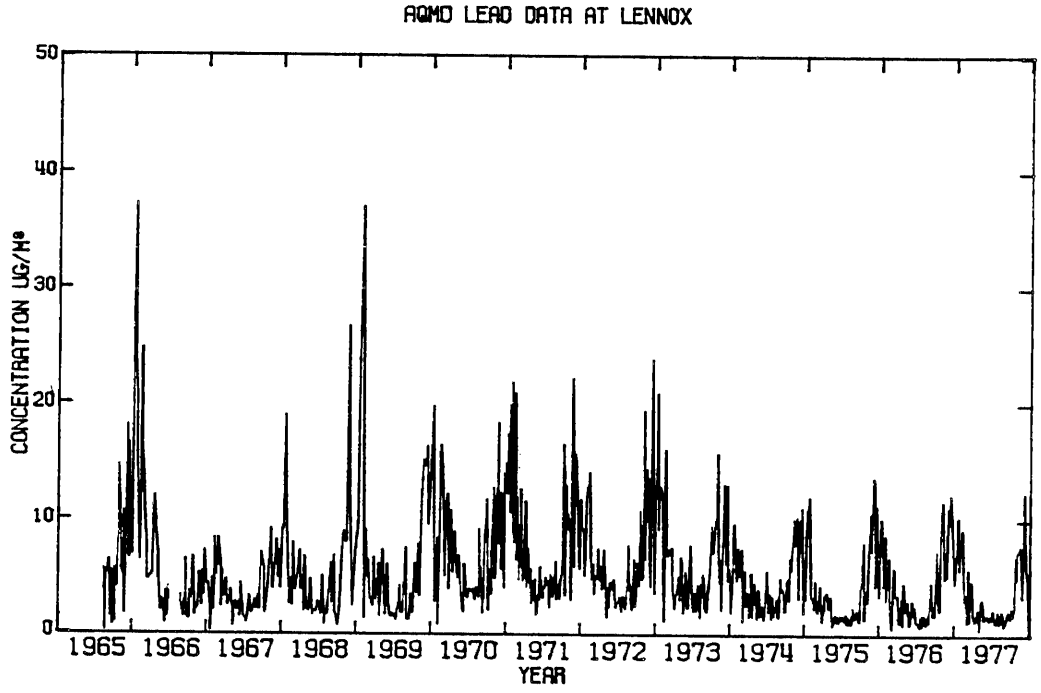



FIGURE A.5.7

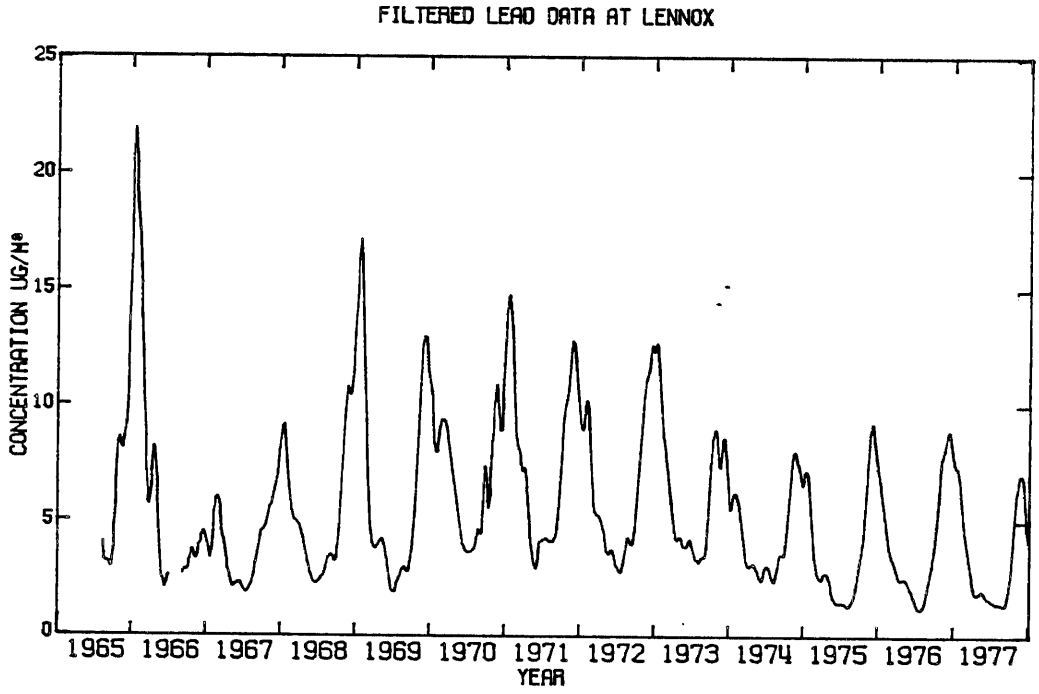



FIGURE A.5.8

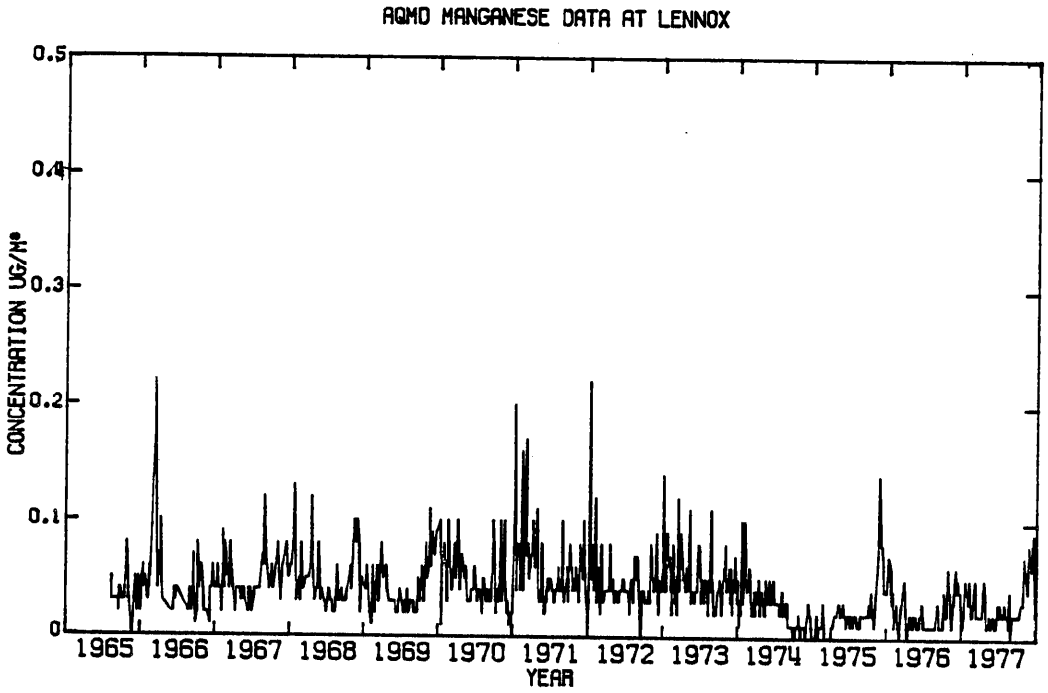



FIGURE A.5.9

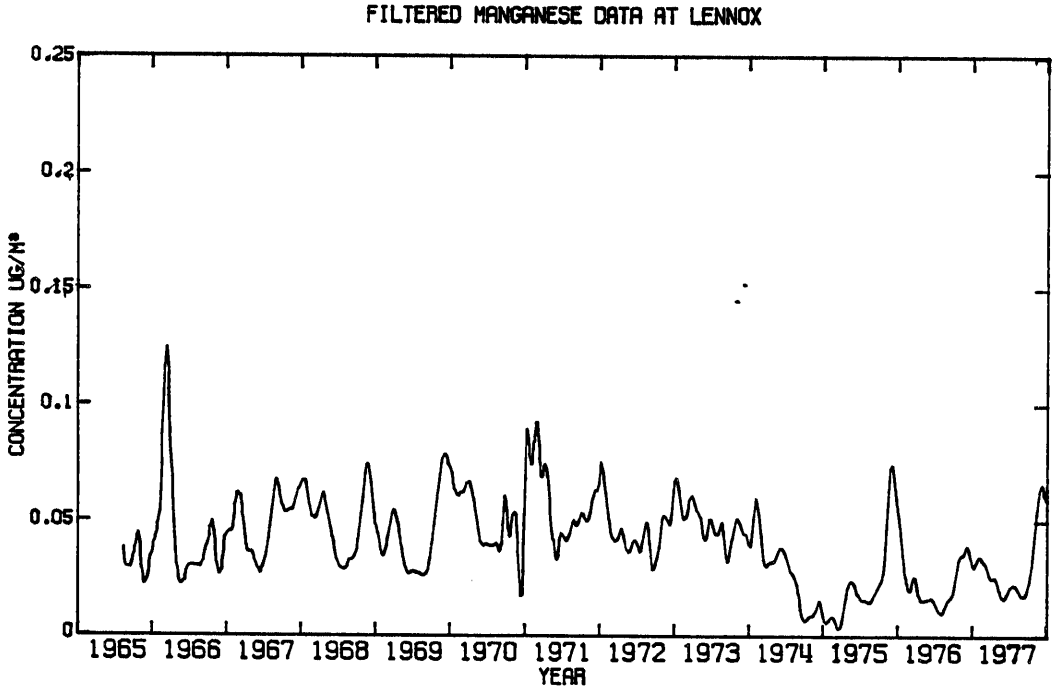



FIGURE A.5.10

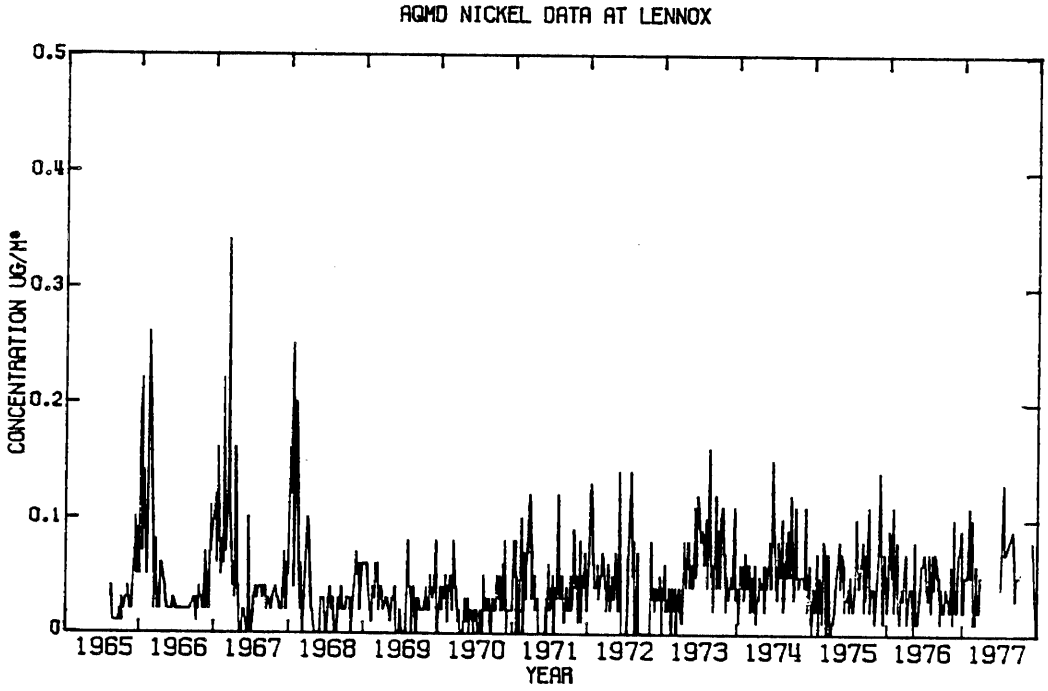



FIGURE A.5.11

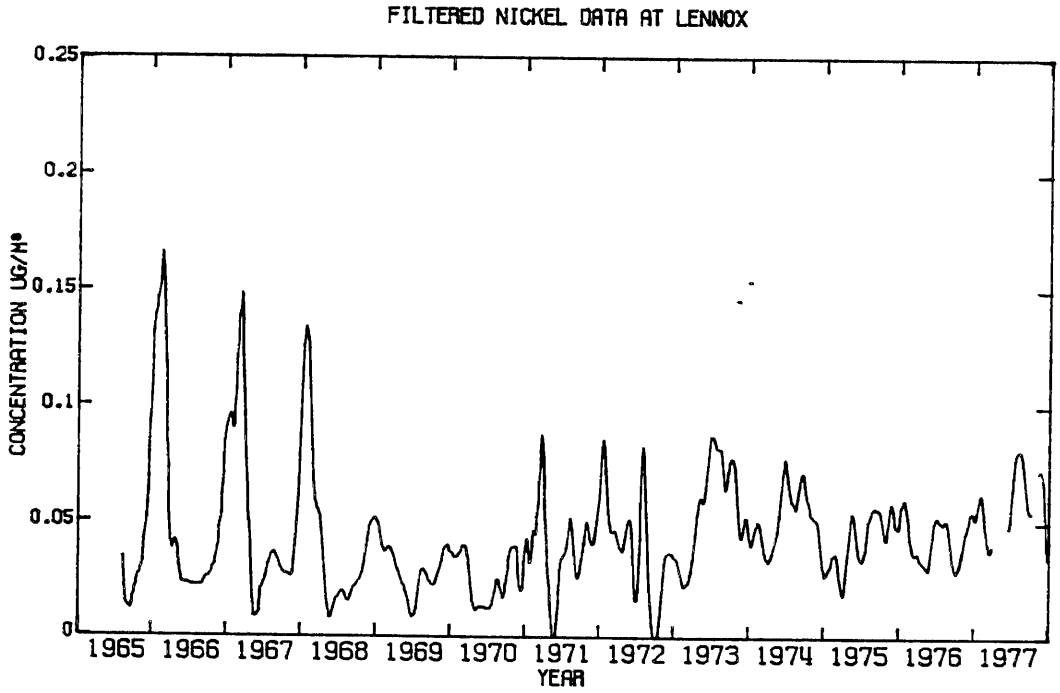



FIGURE A.5.12

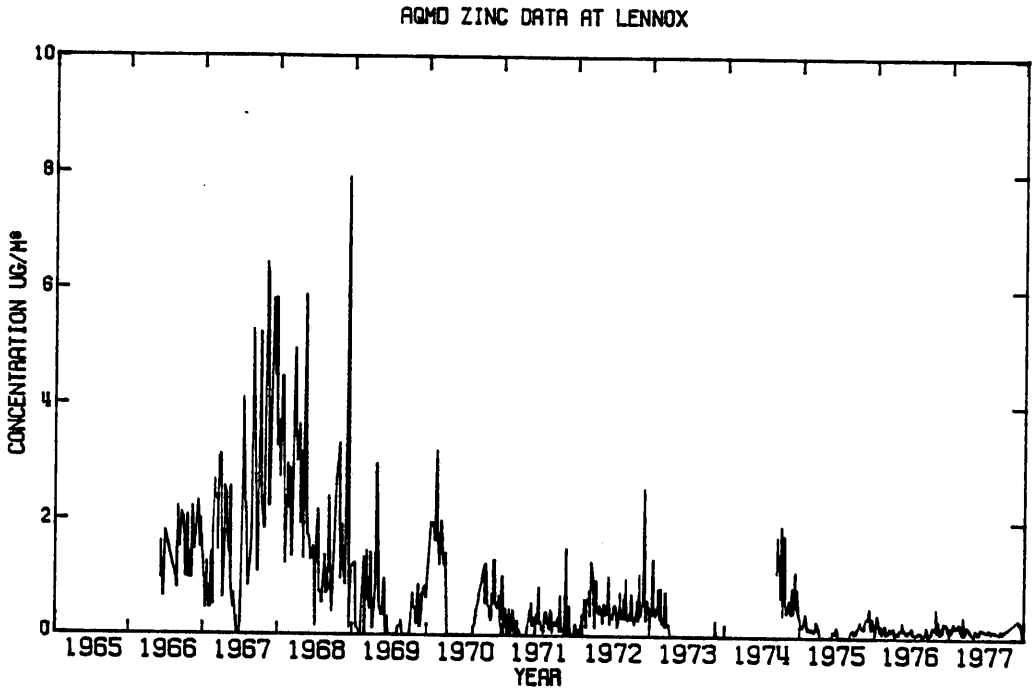



FIGURE A.5.13

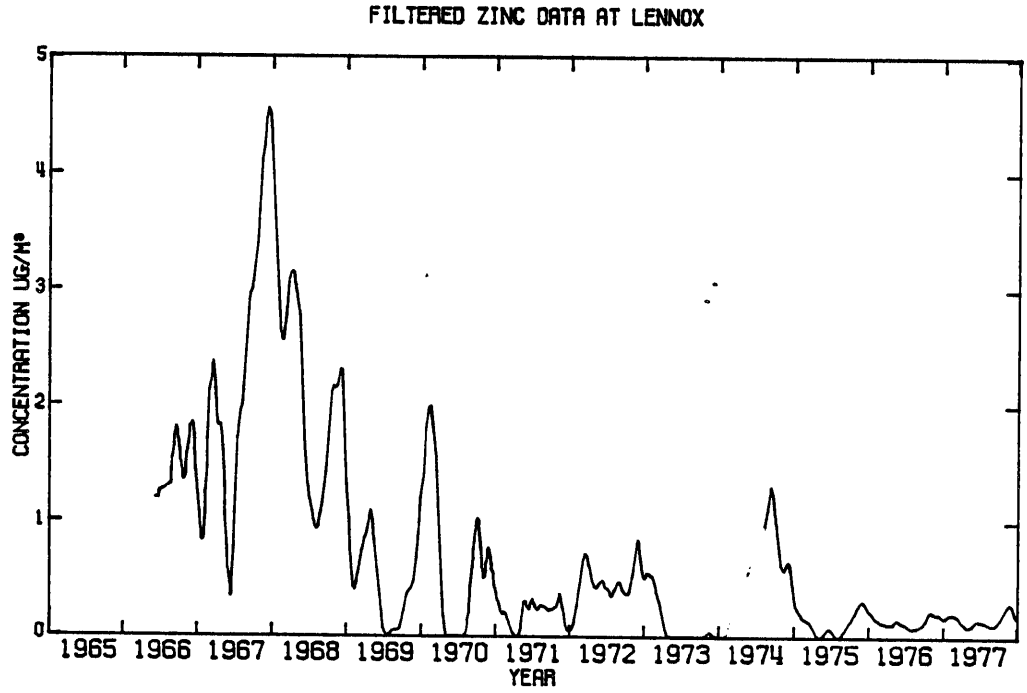



FIGURE A.5.14

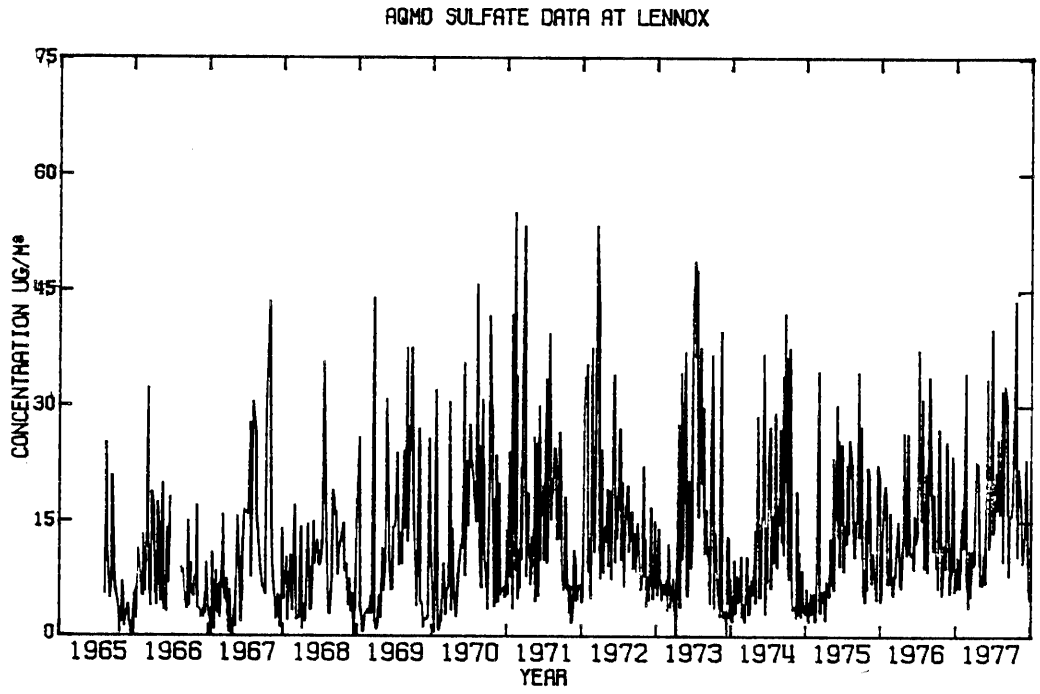



FIGURE A.5.15

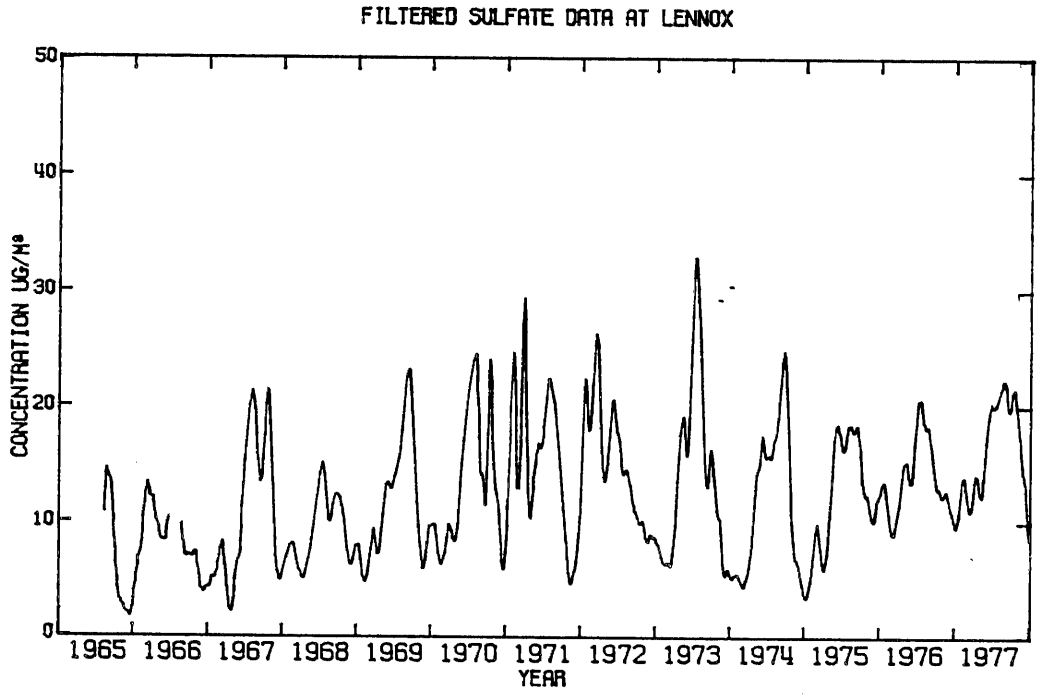



FIGURE A.5.16

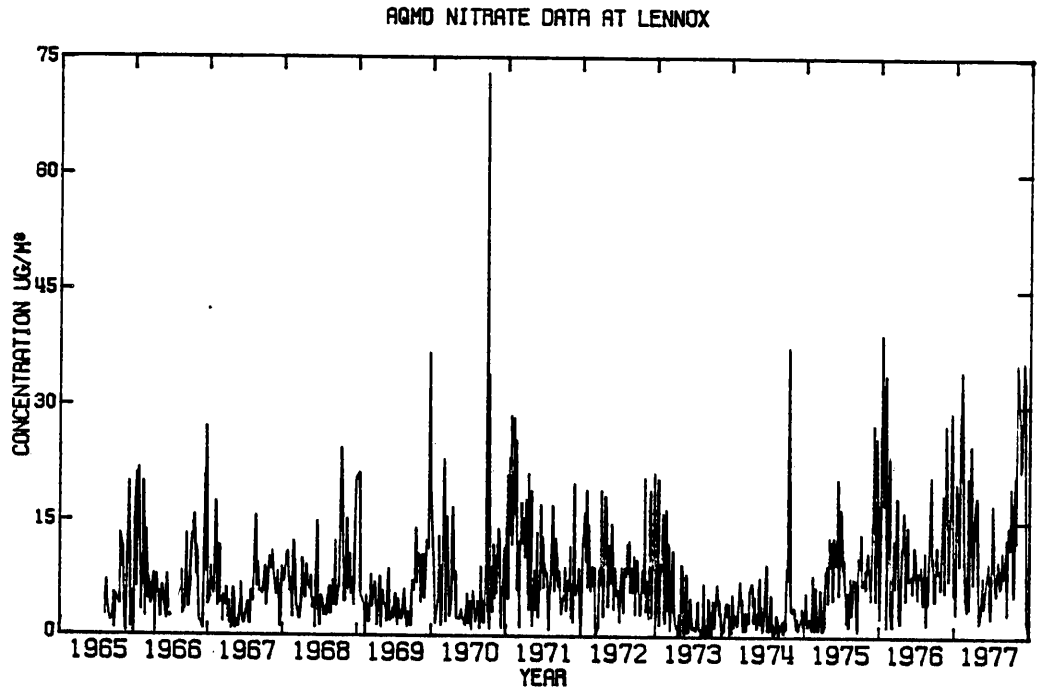



FIGURE A.5.17

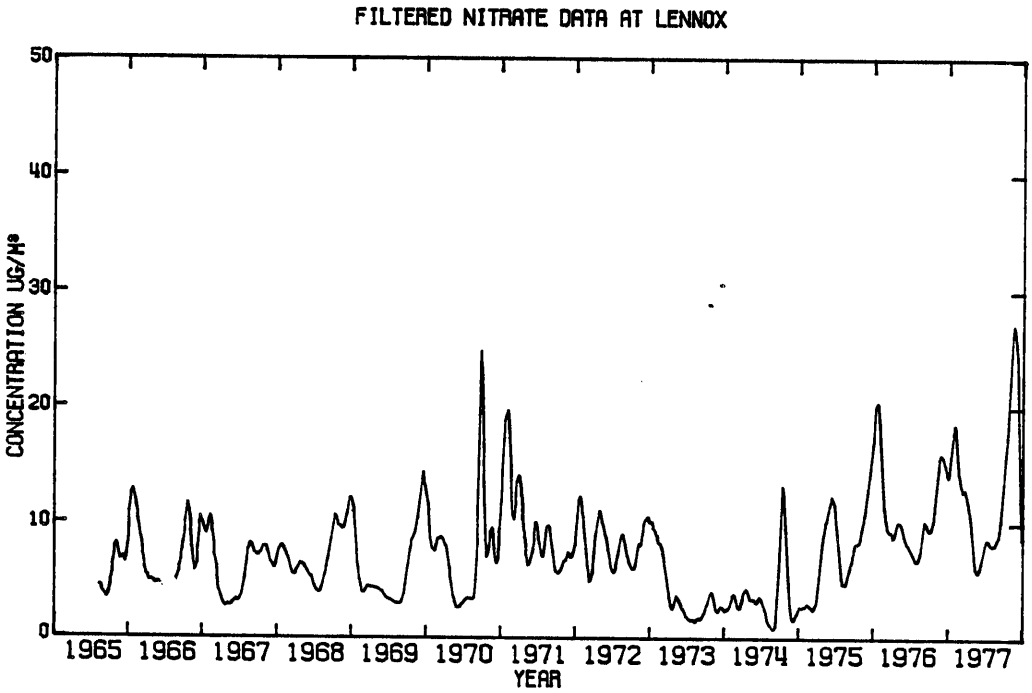



FIGURE A.5.18

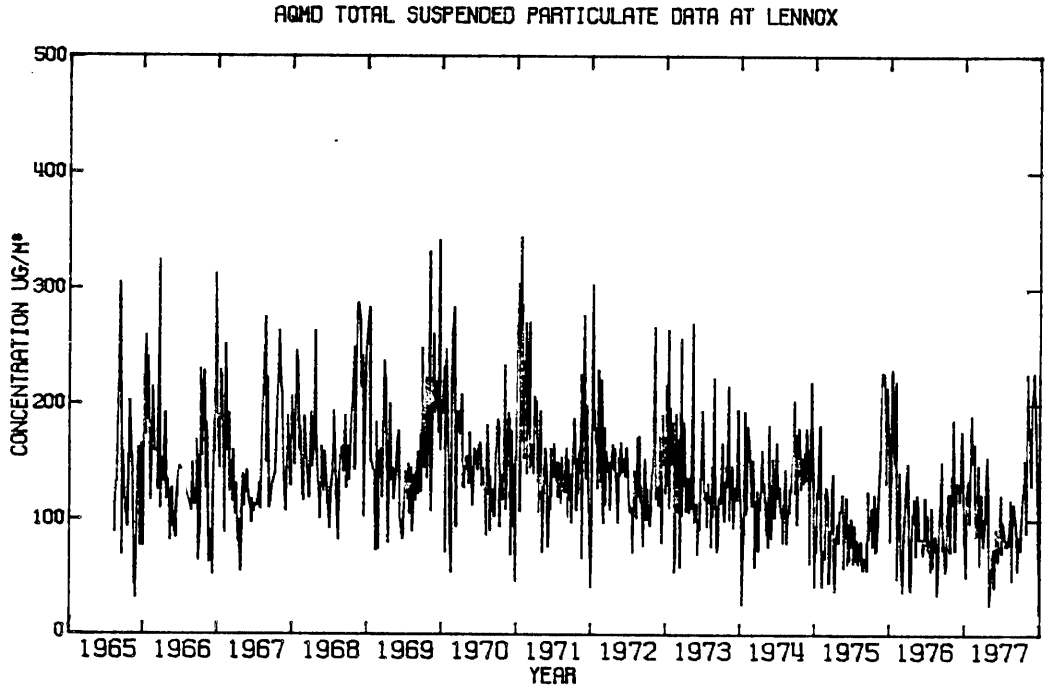



FIGURE A.5.19

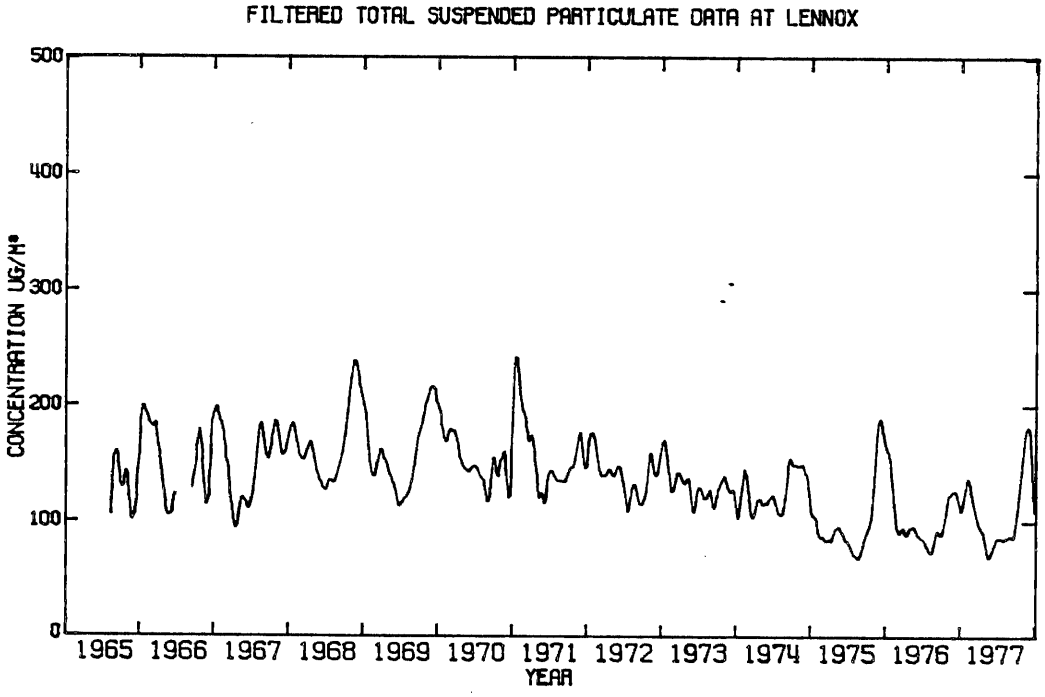



FIGURE A.5.20

## A.6 Monitoring Data at Lynwood Site (SCAQMD)

TABLE A.6.1

Particulate Data Available at Lynwood Monitoring Site (SCAQMD)

| Chemical Species | Figures[a] |
|---|---|
| Chromium | A.6.1 - A.6.2 |
| Copper | A.6.3 - A.6.4 |
| Iron | A.6.5 - A.6.6 |
| Lead | A.6.7 - A.6.8 |
| Manganese | A.6.9 - A.6.10 |
| Nickel | A.6.11 - A.6.12 |
| Zinc | A.6.13 - A.6.14 |
| Sulfates | A.6.15 - A.6.16 |
| Nitrates | A.6.17 - A.6.18 |
| Total Suspended Particulate | A.6.19 - A.6.20 |

a Odd numbered figures correspond to measured data and even numbered ones to filtered results.

TABLE A.6.2

Summary of Particulate Air Quality Statistics
at Lynwood Monitoring Site (SCAQMD)
(Jan 1974 - Dec 1977)

| Chemical Species | Number of Samples | Statistics | | |
|---|---|---|---|---|
| | | Mean | Maximum | Minimum |
| | | (Micrograms $m^{-3}$) | | |
| Chromium | 221 | 0.01 | 0.04 | 0.00 |
| Copper | 227 | 0.47 | 1.33 | 0.00 |
| Iron | 211 | 1.73 | 7.02 | 0.00 |
| Lead | 247 | 2.56 | 12.0 | 0.53 |
| Manganese | 247 | 0.037 | 0.11 | 0.00 |
| Nickel | 223 | 0.035 | 0.17 | 0.00 |
| Zinc | 218 | 0.188 | 0.98 | 0.00 |
| Sulfates | 247 | 11.09 | 41.7 | 1.10 |
| Nitrates | 247 | 9.05 | 41.7 | 0.10 |
| TSP | 248 | 106.06 | 315.5 | 20.50 |

Note: All samples are 24 hour averages

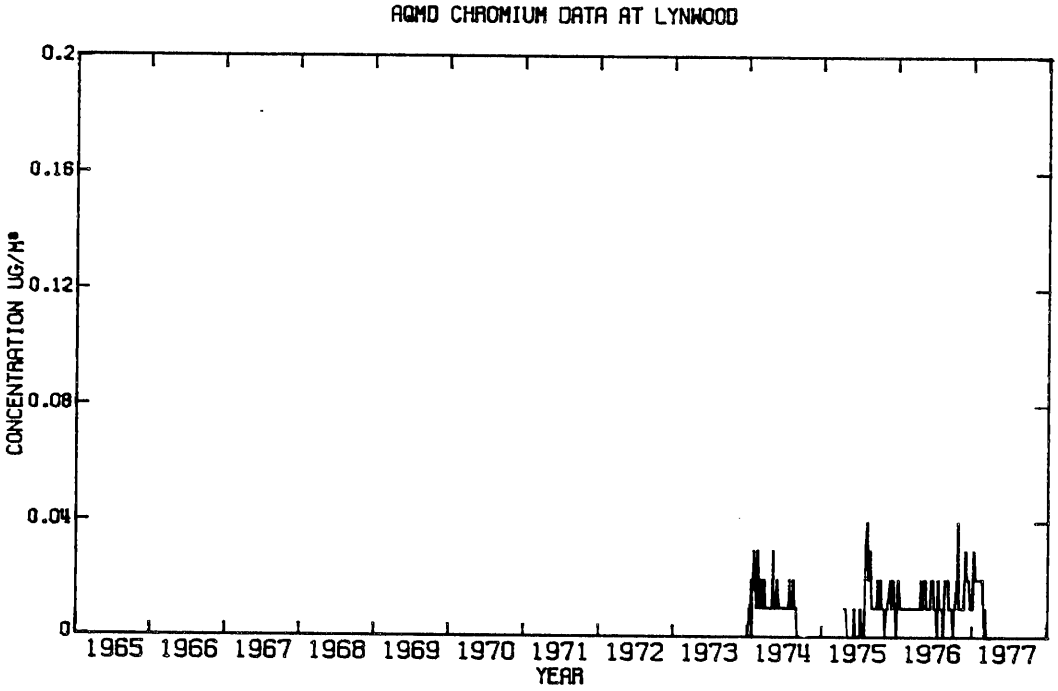



FIGURE A.6.1

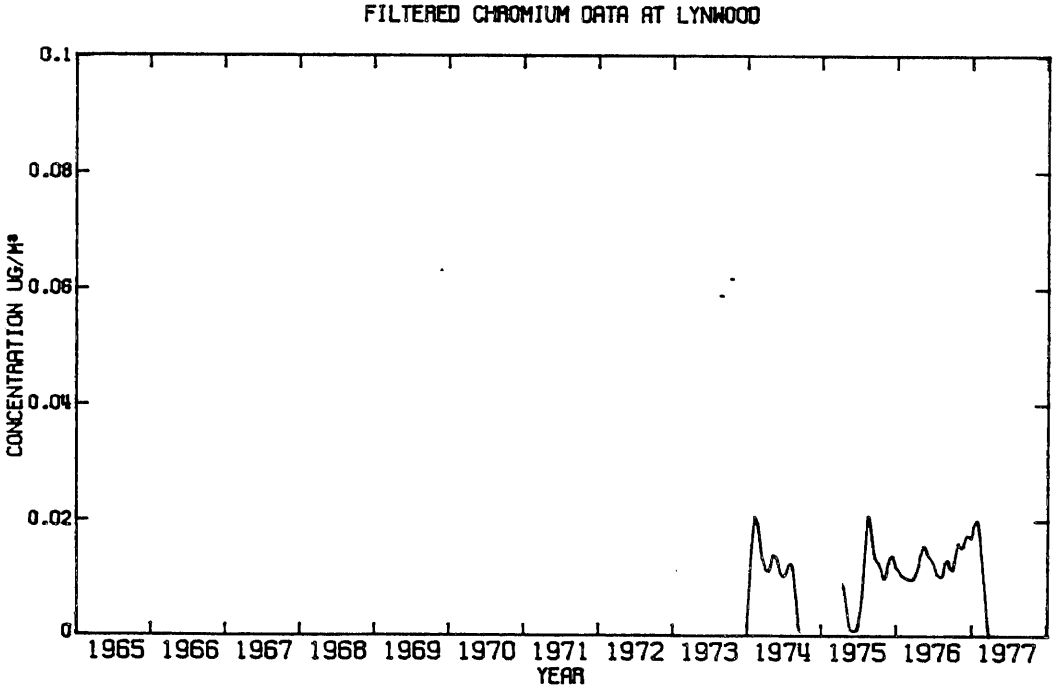



FIGURE A.6.2

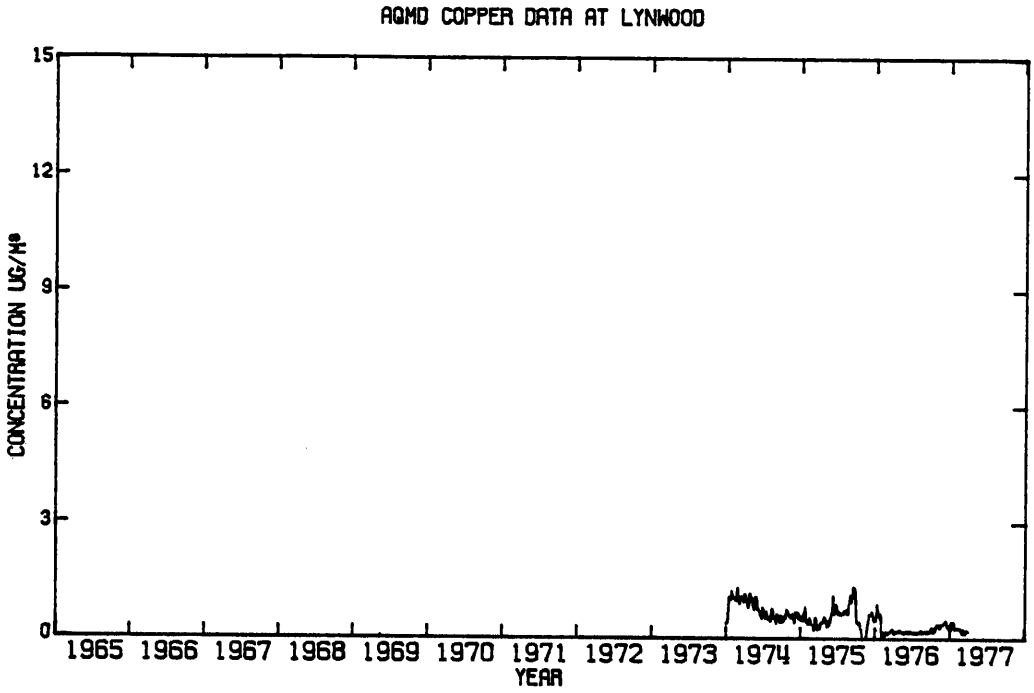



FIGURE A.6.3

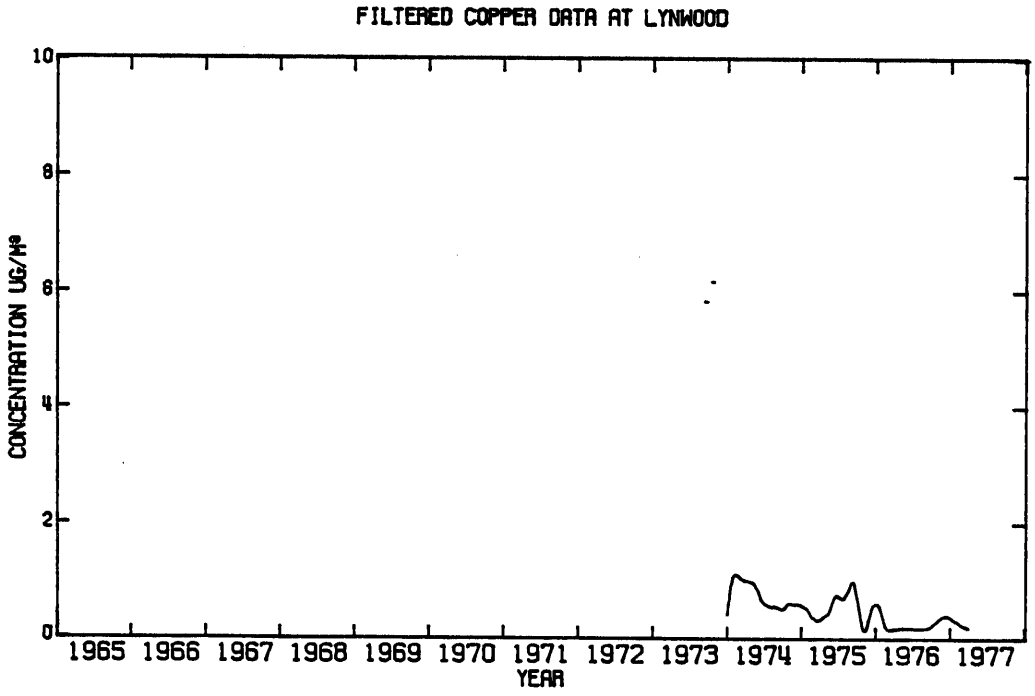



FIGURE A.6.4

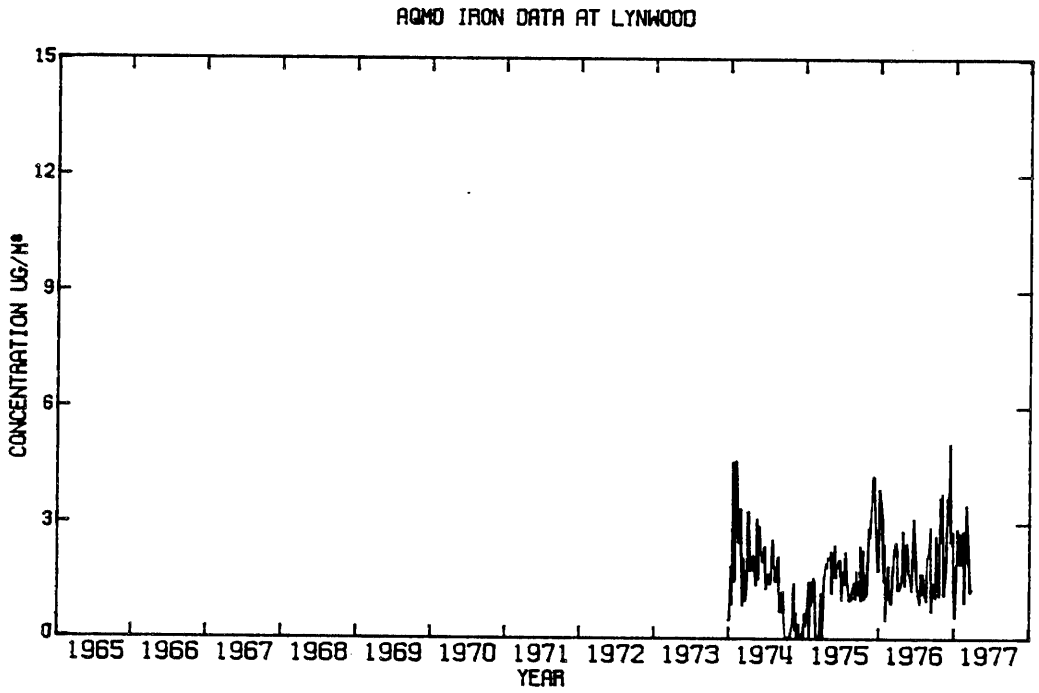



FIGURE A.6.5

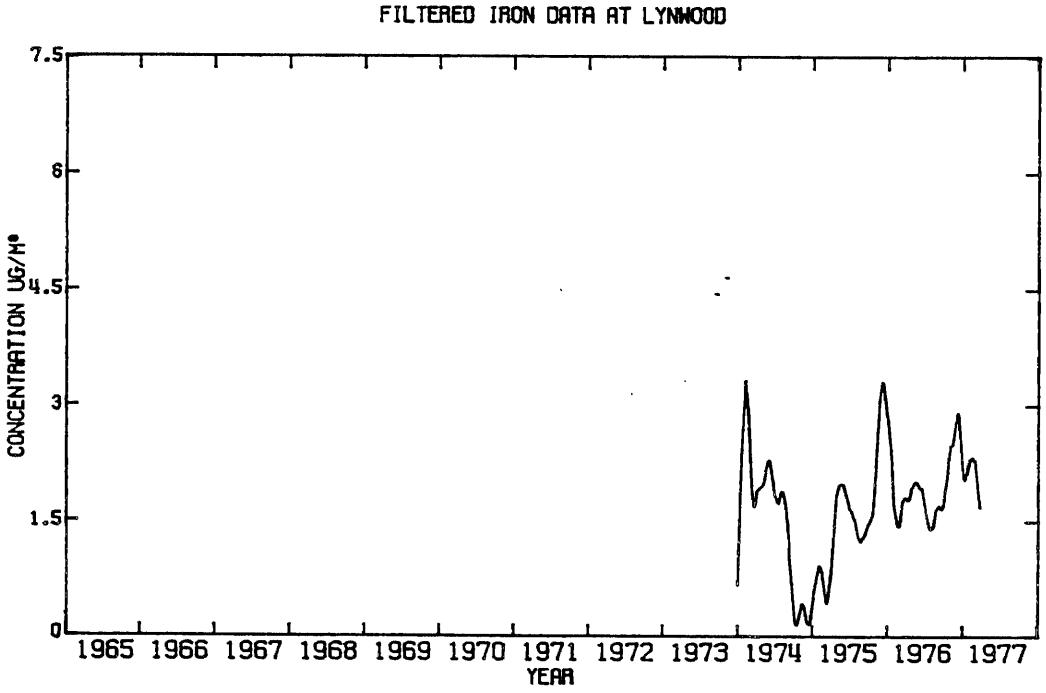



FIGURE A.6.6

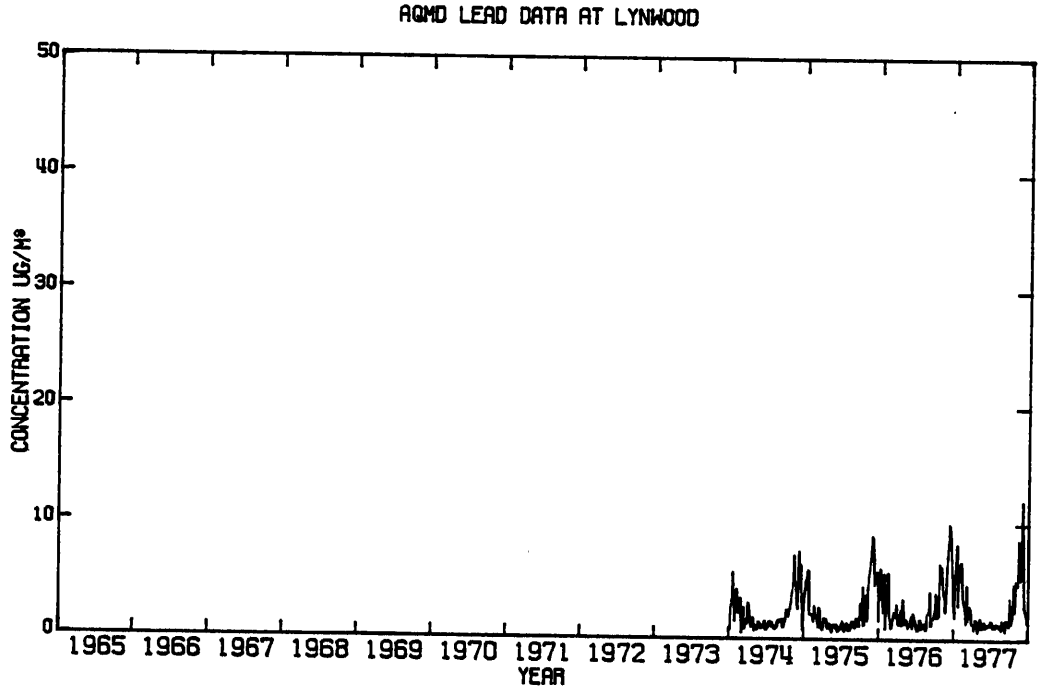



FIGURE A.6.7

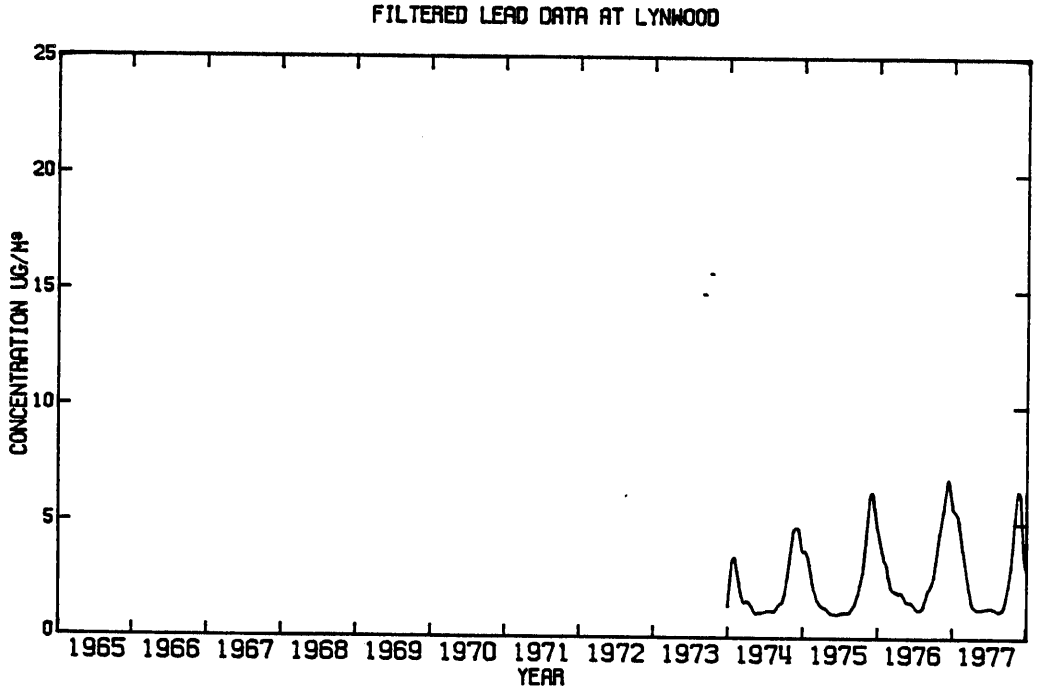



FIGURE A.6.8

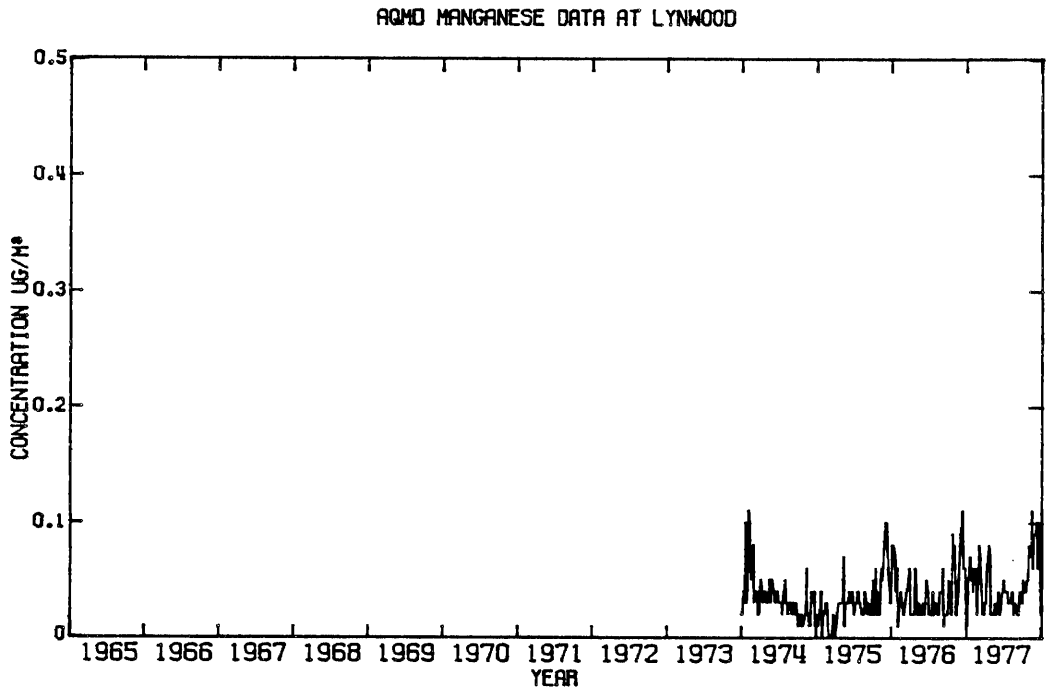



FIGURE A.6.9

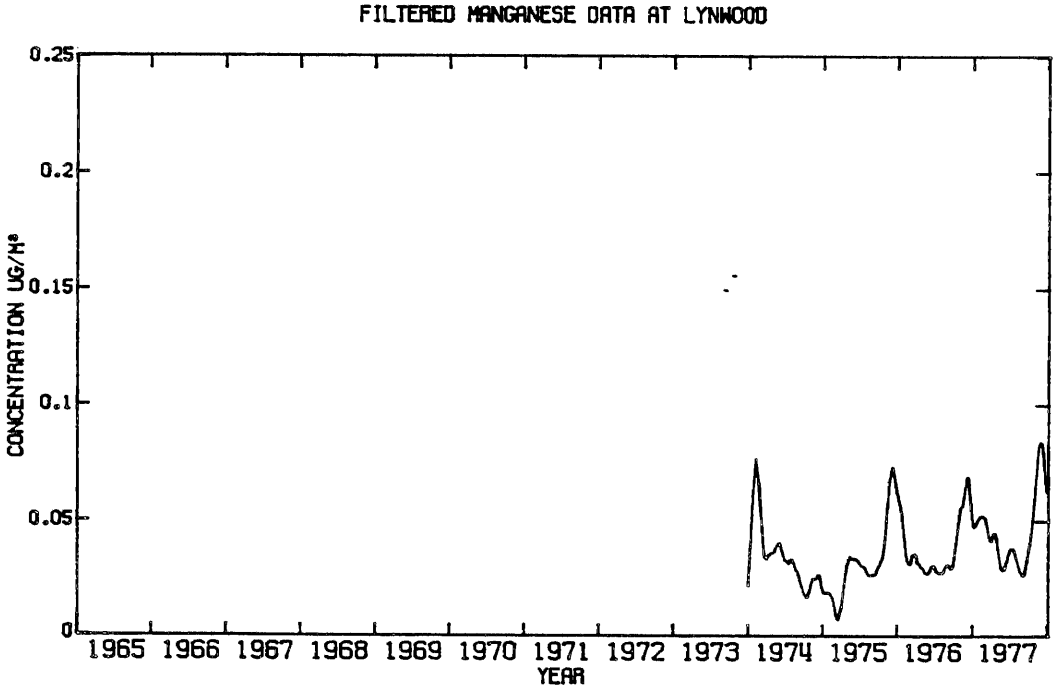



FIGURE A.6.10

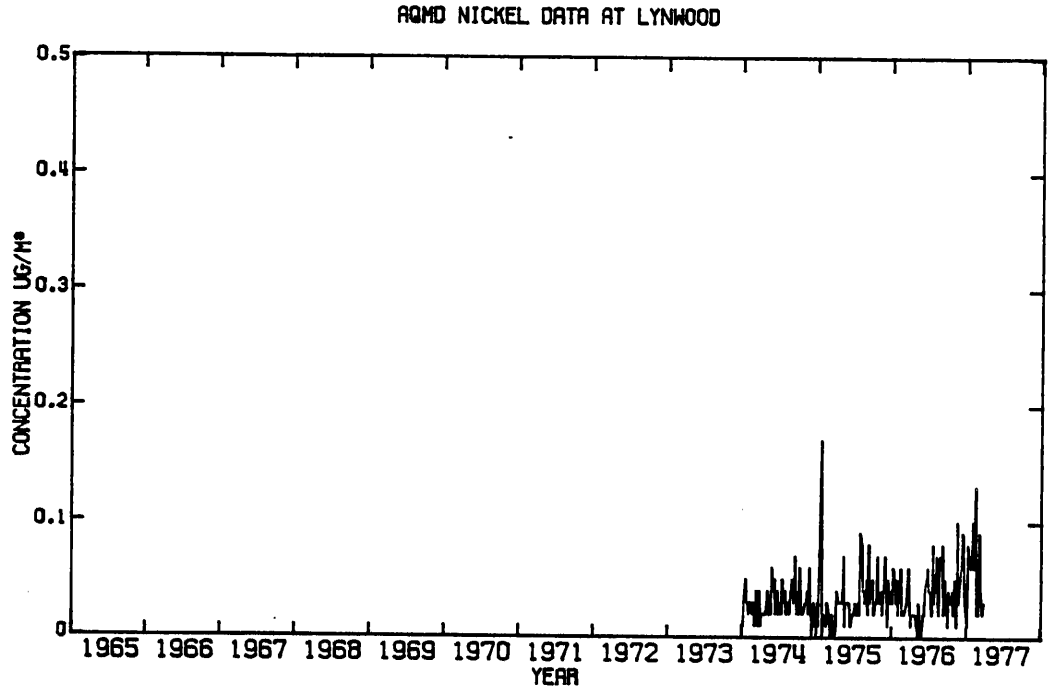



FIGURE A.6.11

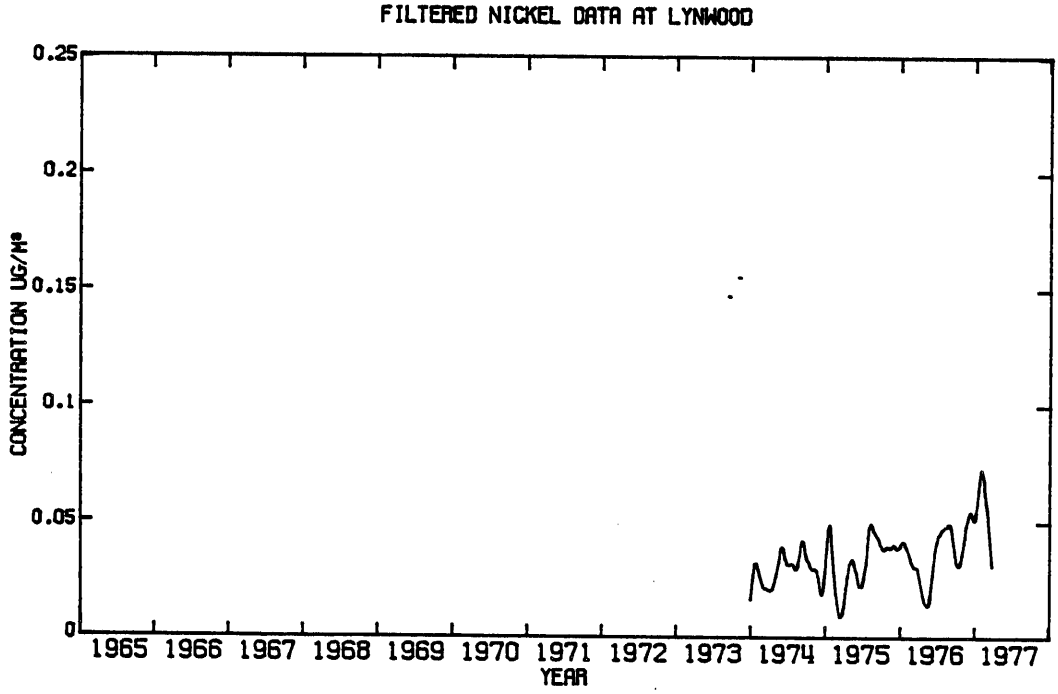



FIGURE A.6.12

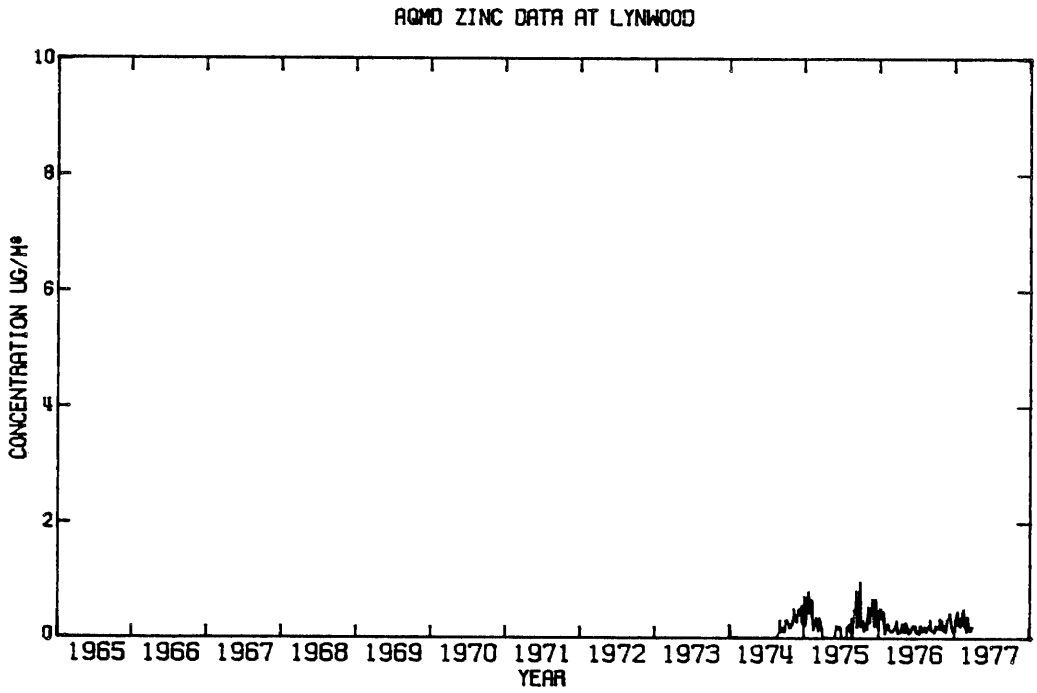



FIGURE A.6.13

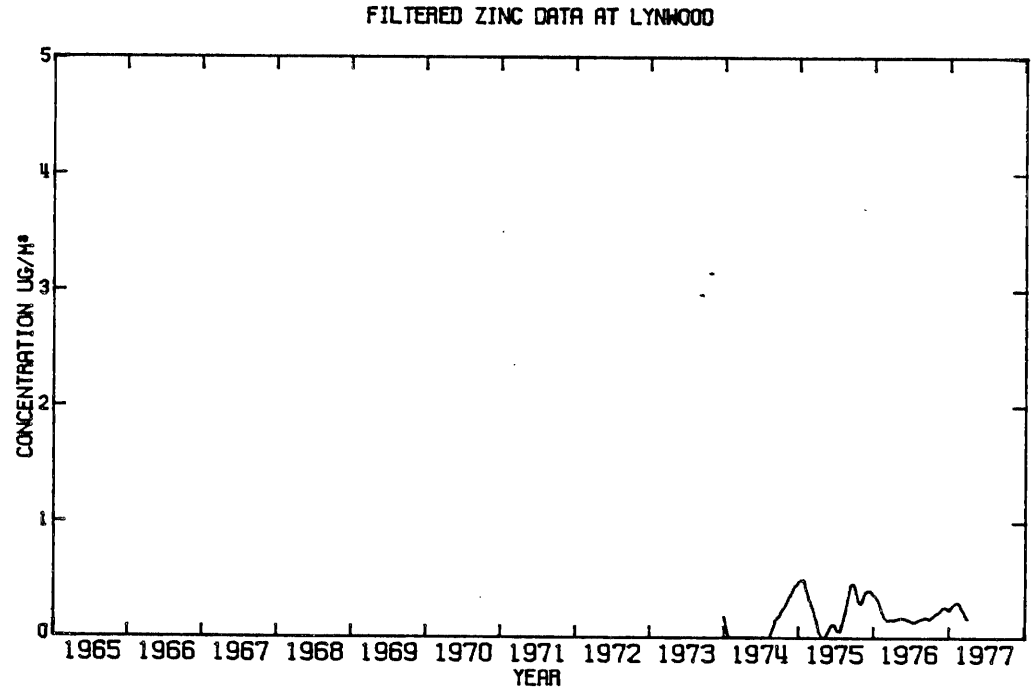



FIGURE A.6.14

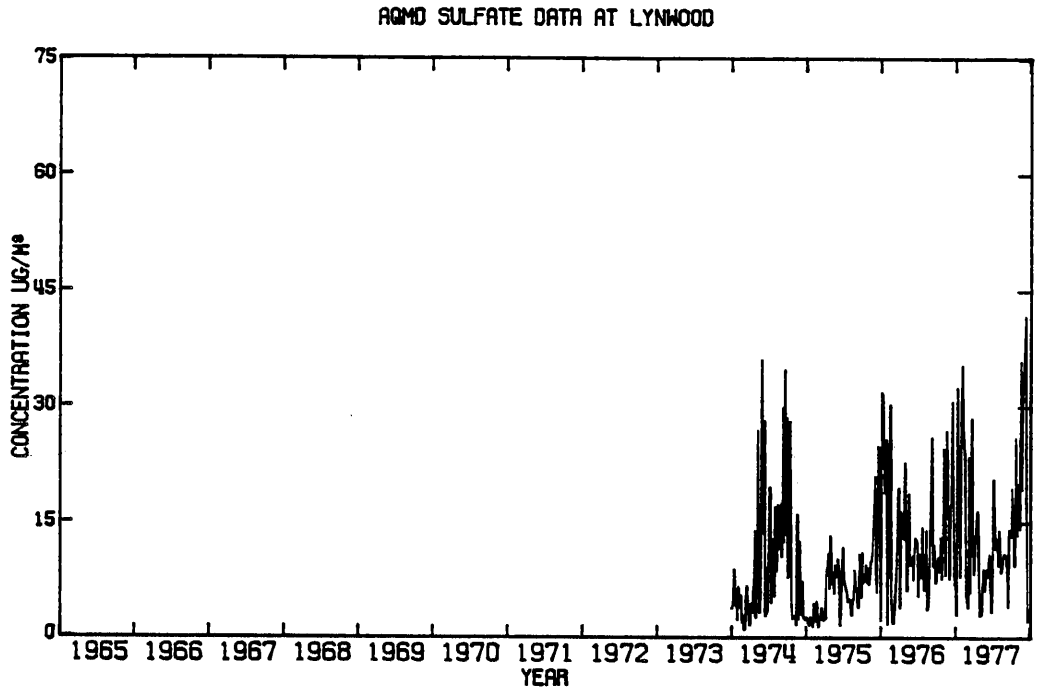



FIGURE A.6.15

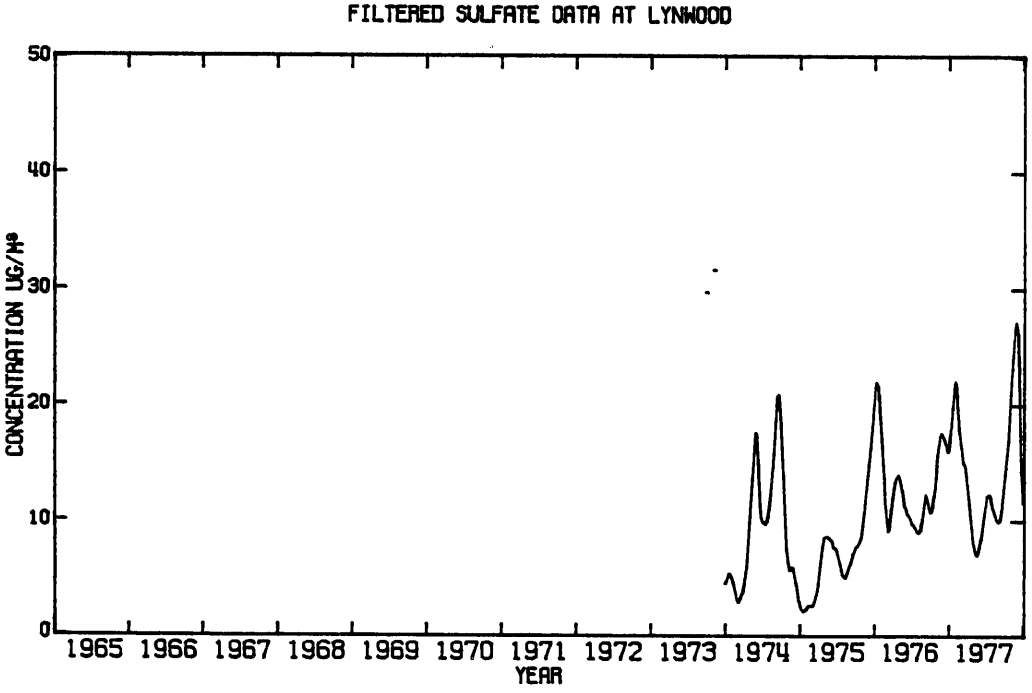



FIGURE A.6.16

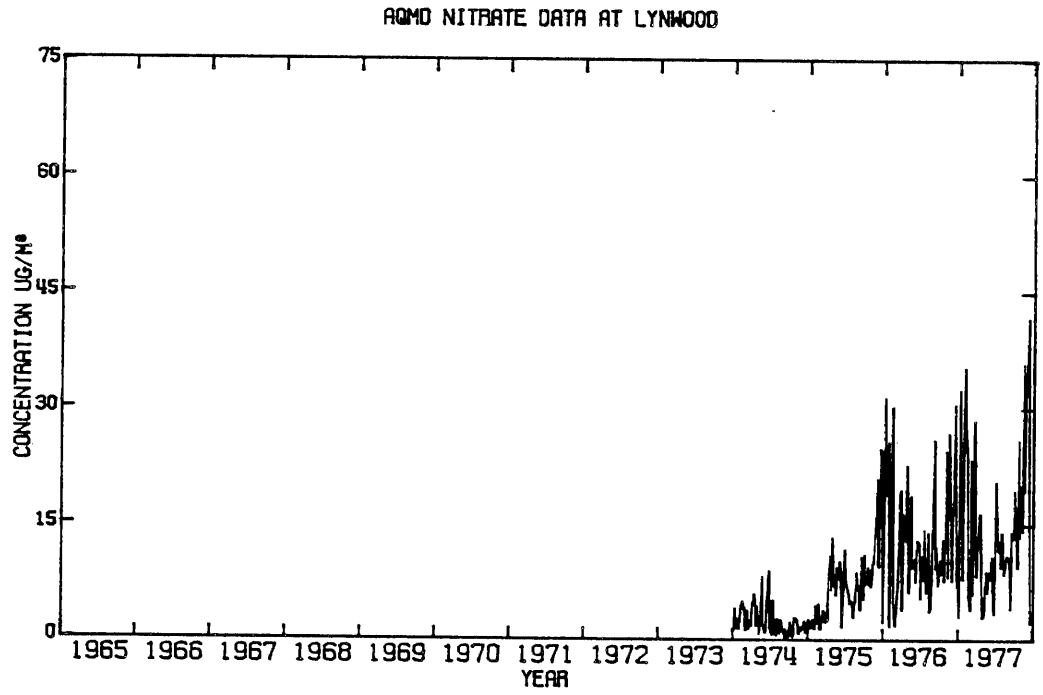



FIGURE A.6.17

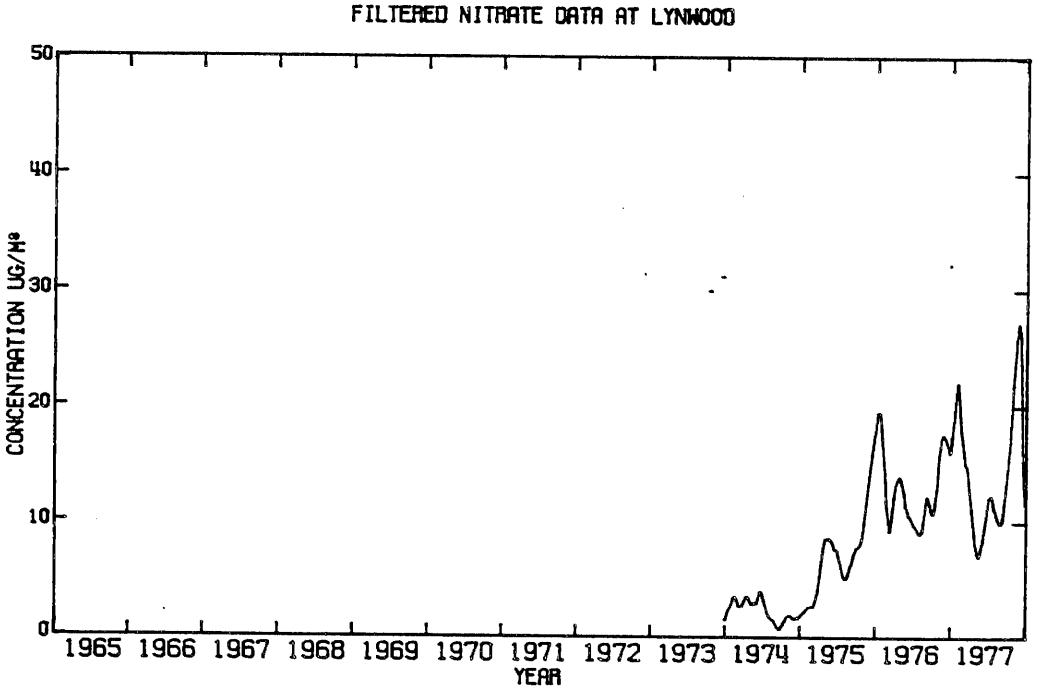



FIGURE A.6.18

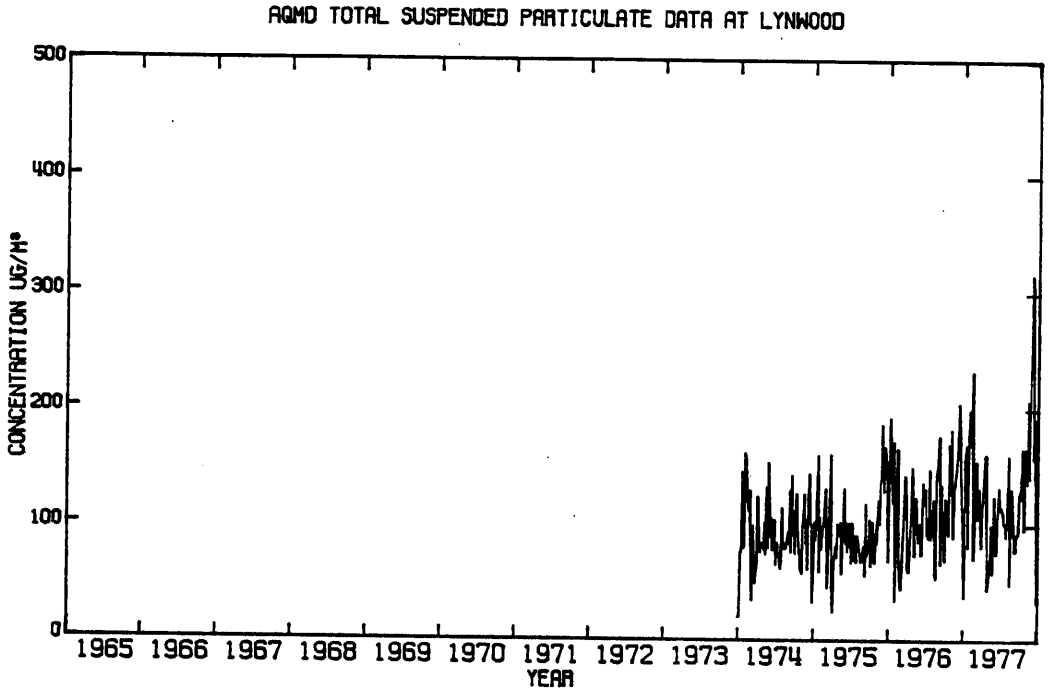



FIGURE A.6.19

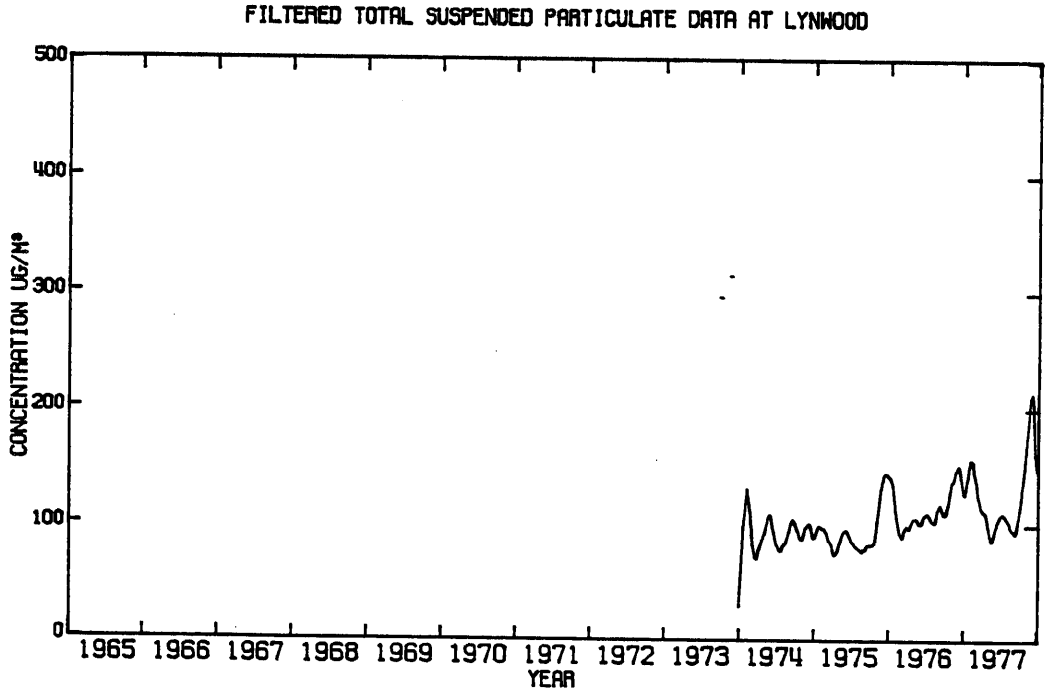



FIGURE A.6.20

## A.7 Monitoring Data at Pasadena Site (SCAQMD)

TABLE A.7.1

Particulate Data Available at Pasadena Monitoring Site (SCAQMD)

| Chemical Species | Figures[a] |
|---|---|
| Chromium | A.7.1 - A.7.2 |
| Copper | A.7.3 - A.7.4 |
| Iron | A.7.5 - A.7.6 |
| Lead | A.7.7 - A.7.8 |
| Manganese | A.7.9 - A.7.10 |
| Nickel | A.7.11 - A.7.12 |
| Zinc | A.7.13 - A.7.14 |
| Sulfates | A.7.15 - A.7.16 |
| Nitrates | A.7.17 - A.7.18 |
| Total Suspended Particulate | A.7.19 - A.7.20 |

a Odd numbered figures correspond to measured data and even numbered ones to filtered results.

TABLE A.7.2

Summary of Particulate Air Quality Statistics
at Pasadena Monitoring Site (SCAQMD)
(Jul 1971 - Dec 1977)

| Chemical Species | Number of Samples | Statistics | | |
|---|---|---|---|---|
| | | Mean | Maximum | Minimum |
| | | (Micrograms $m^{-3}$) | | |
| Chromium | 402 | 0.009 | 0.11 | 0.00 |
| Copper | 413 | 0.40 | 2.27 | 0.02 |
| Iron | 392 | 1.77 | 25.11 | 0.00 |
| Lead | 433 | 2.83 | 9.55 | 0.44 |
| Manganese | 392 | 0.040 | 0.66 | 0.00 |
| Nickel | 402 | 0.022 | 0.10 | 0.00 |
| Zinc | 403 | 0.15 | 1.42 | 0.00 |
| Sulfates | 433 | 11.20 | 48.4 | 0.10 |
| Nitrates | 433 | 9.28 | 62.30 | 0.10 |
| TSP | 434 | 108.0 | 624.0 | 12.00 |

Note: All samples are 24 hour averages

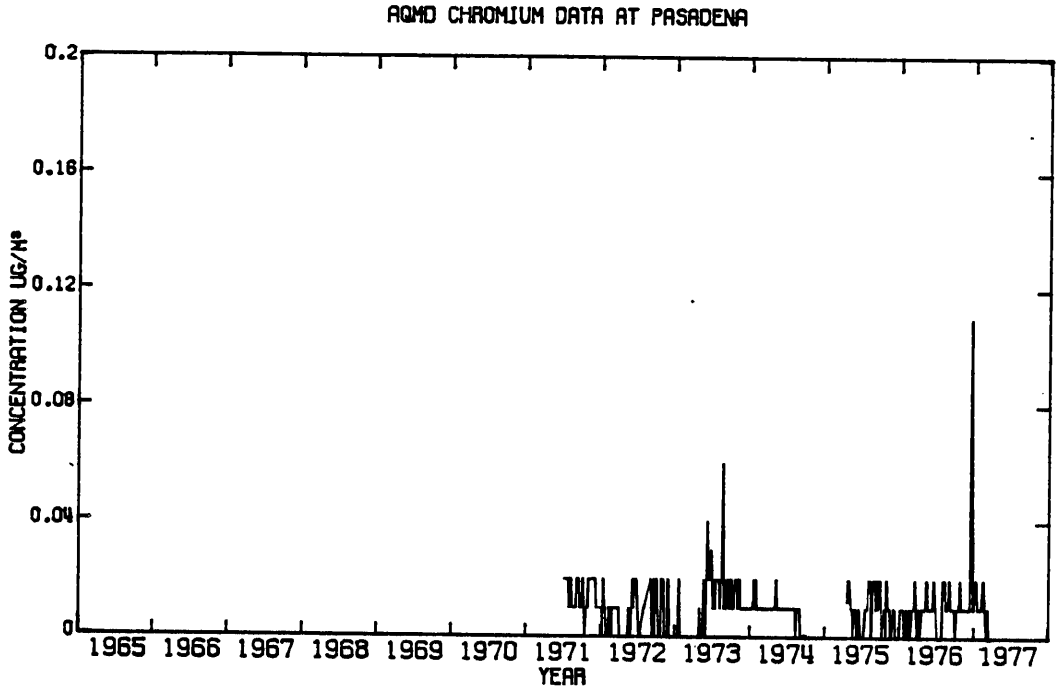



FIGURE A.7.1

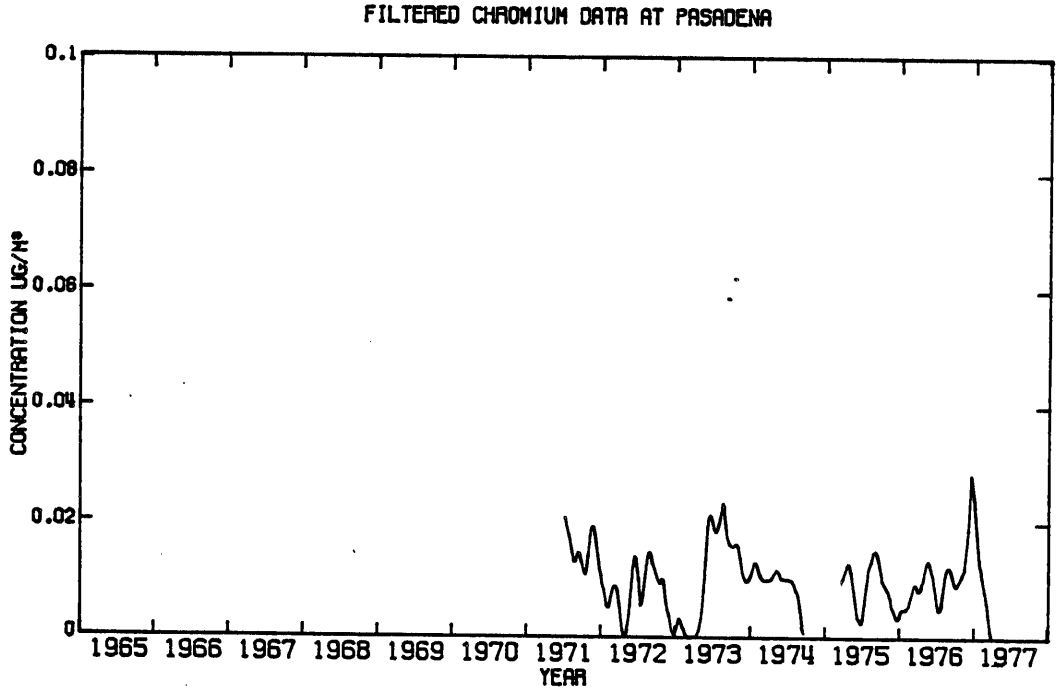



FIGURE A.7.2

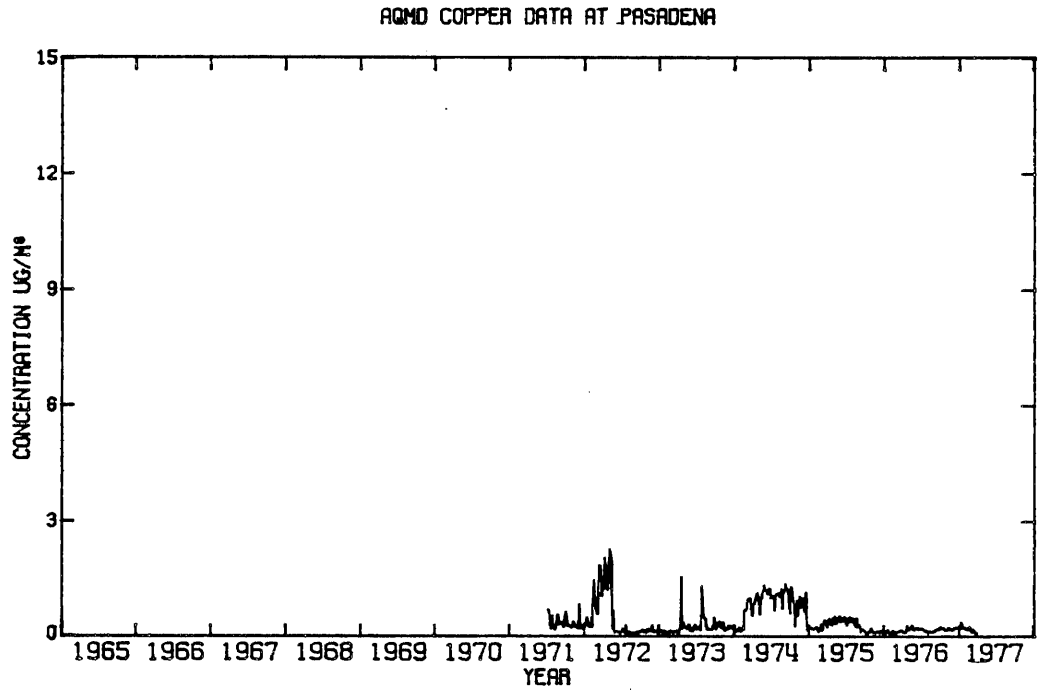



FIGURE A.7.3

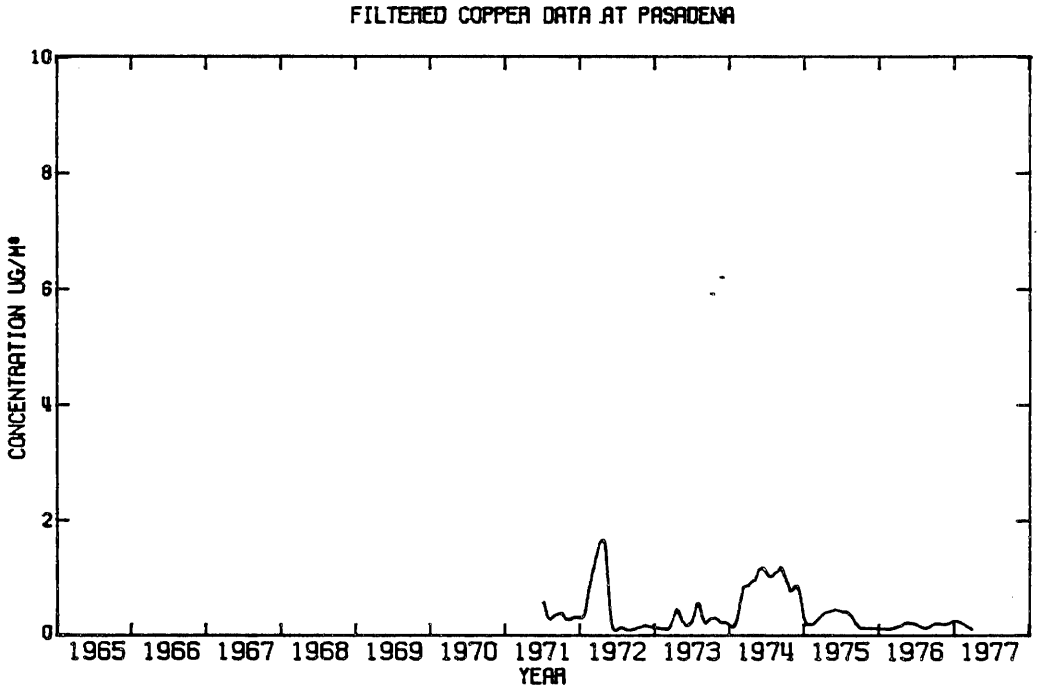



FIGURE A.7.4

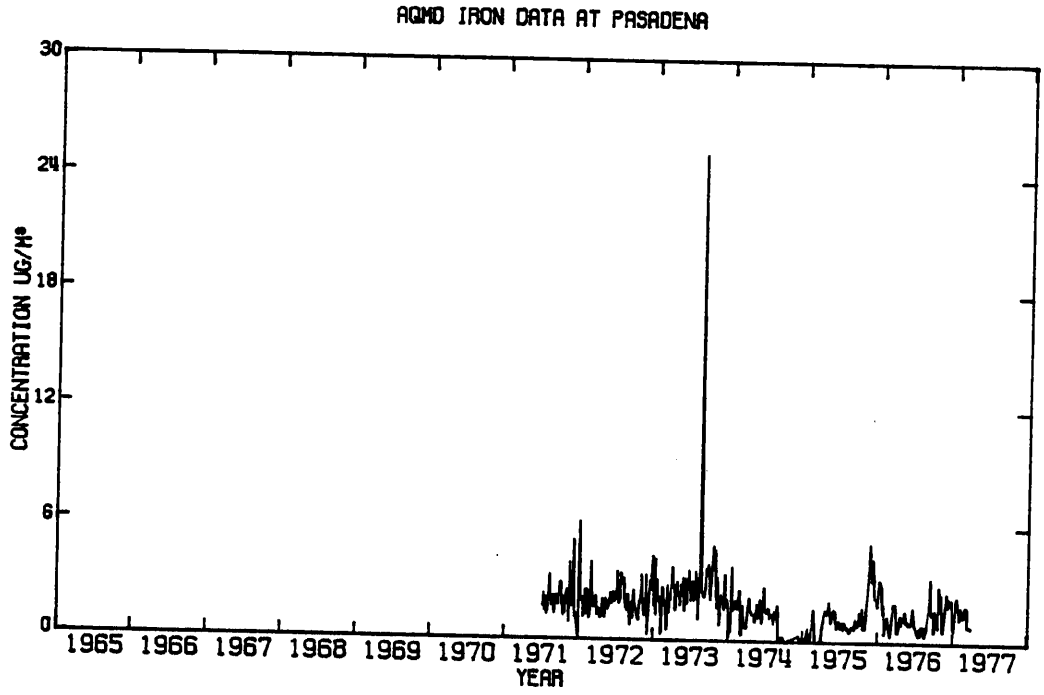



FIGURE A.7.5

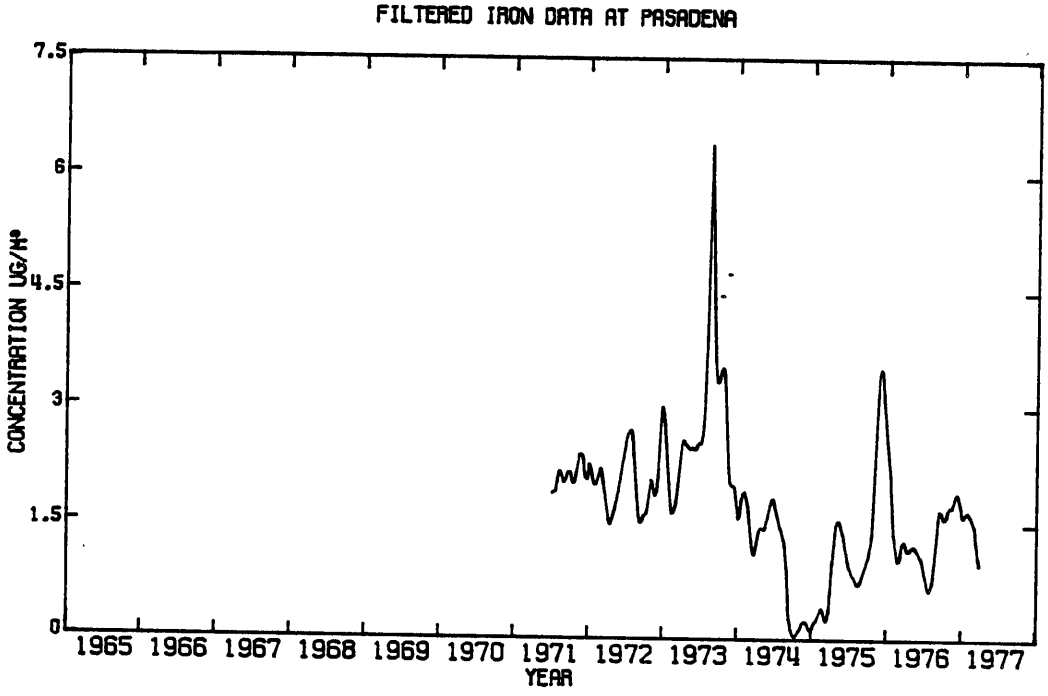



FIGURE A.7.6

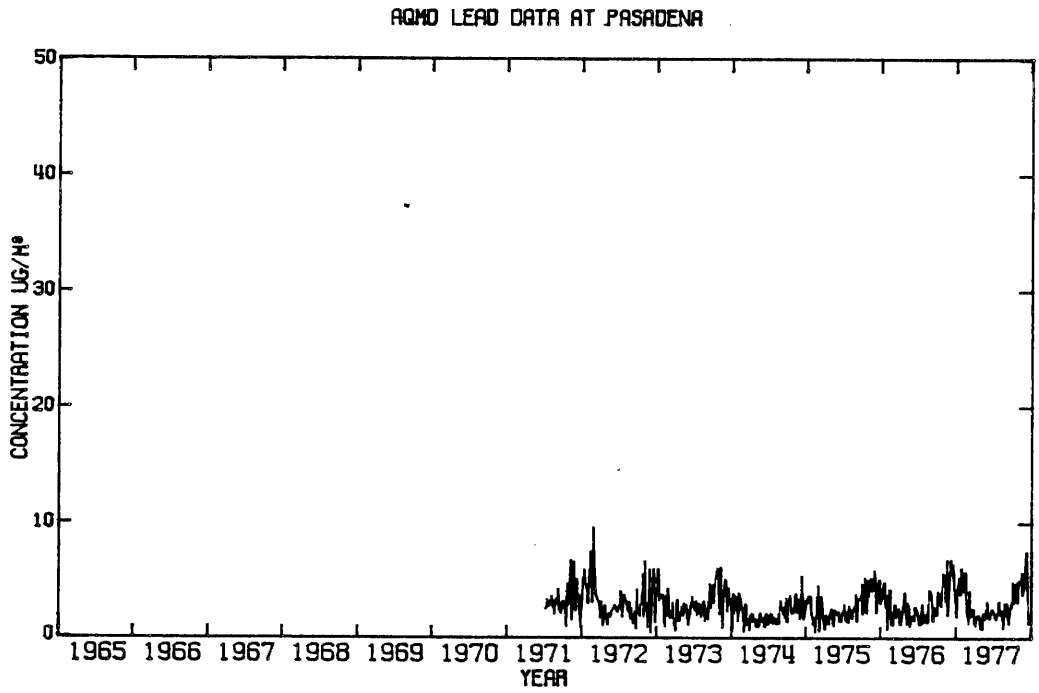



FIGURE A.7.7

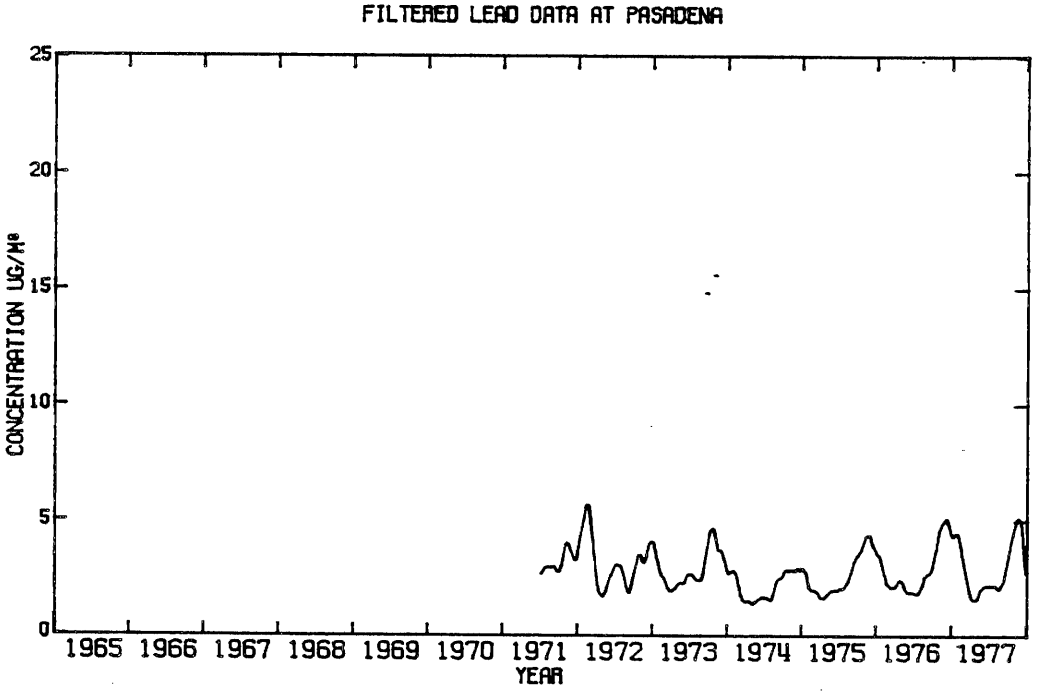



FIGURE A.7.8

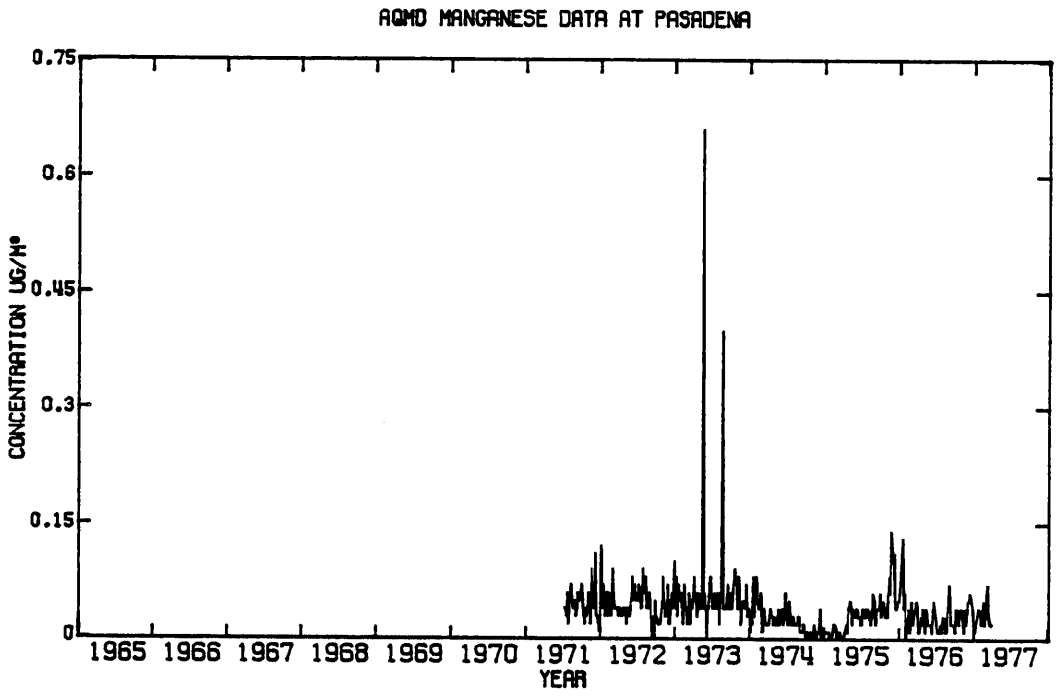



FIGURE A.7.9

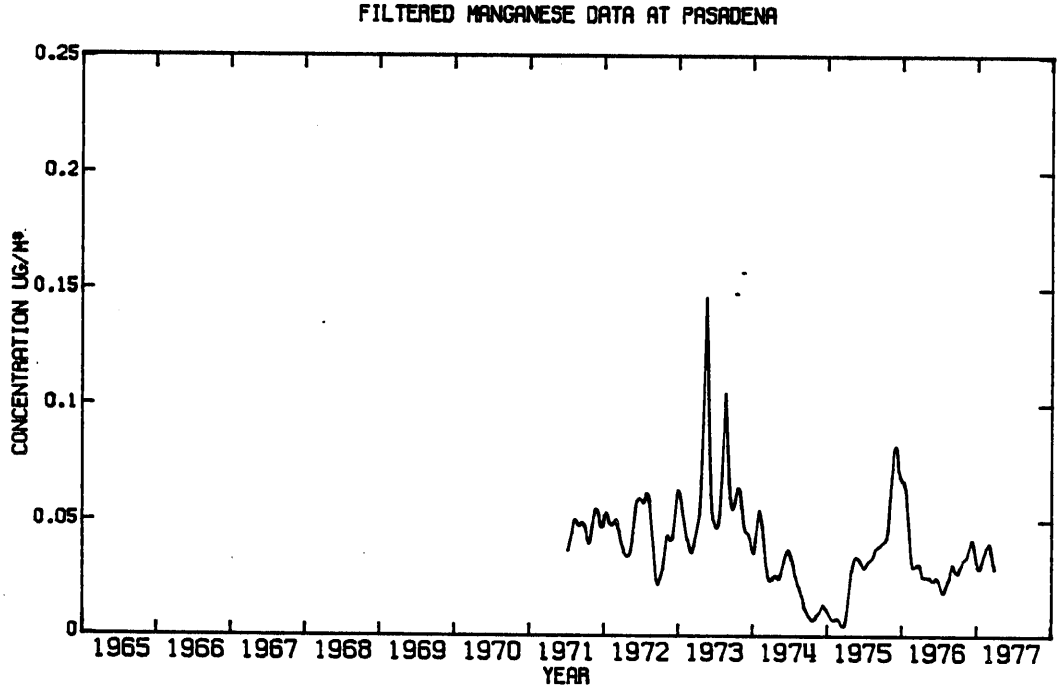



FIGURE A.7.10

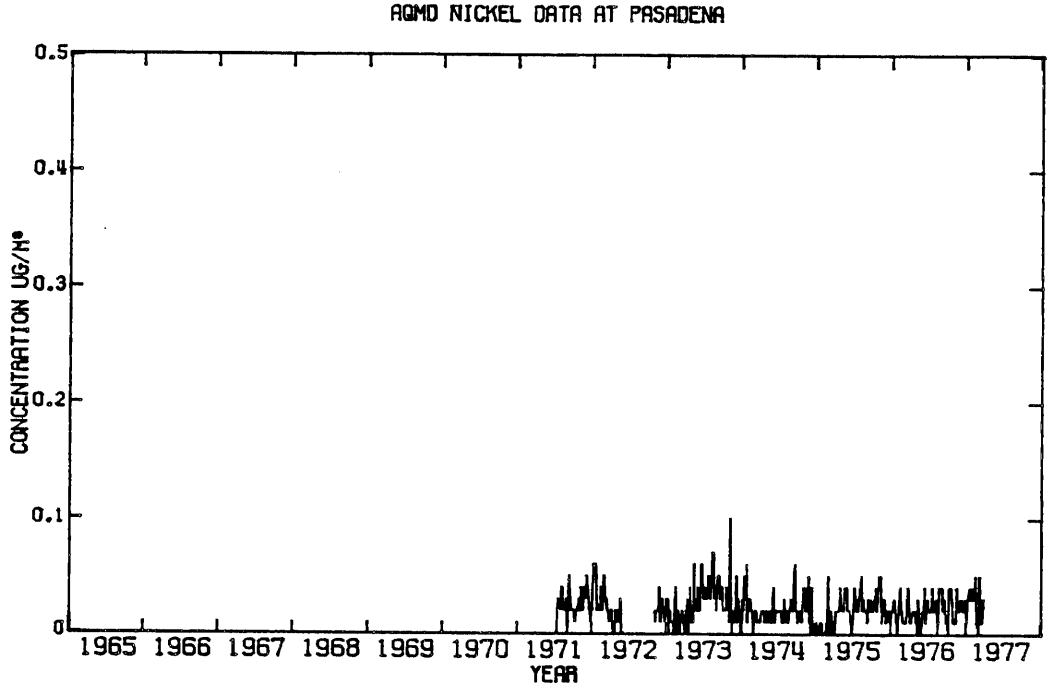



FIGURE A.7.11

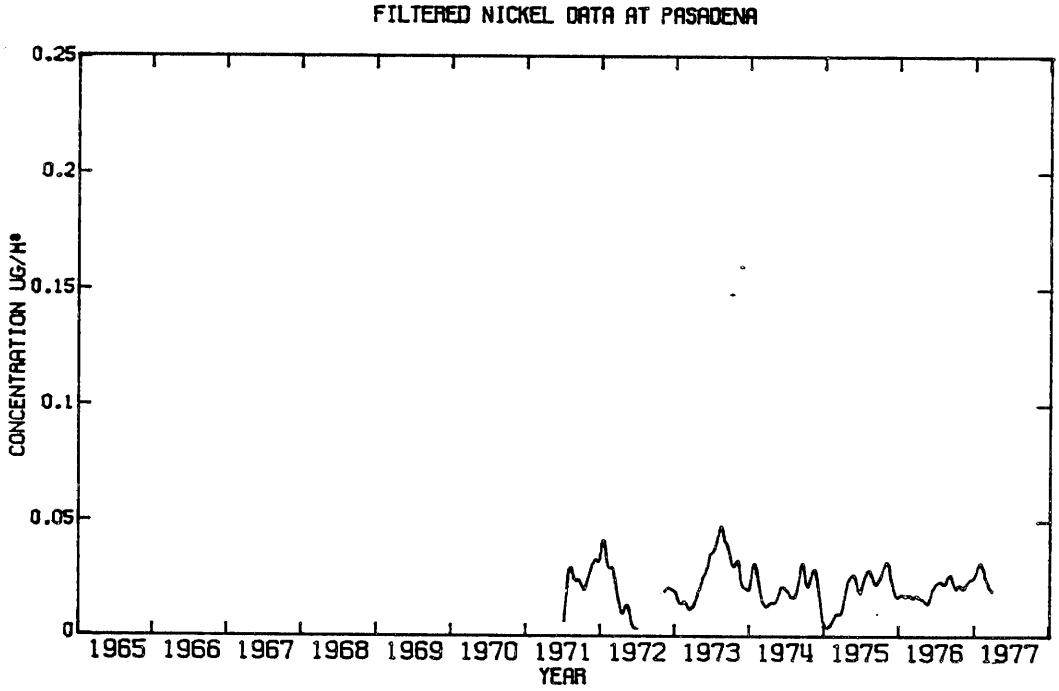



FIGURE A.7.12

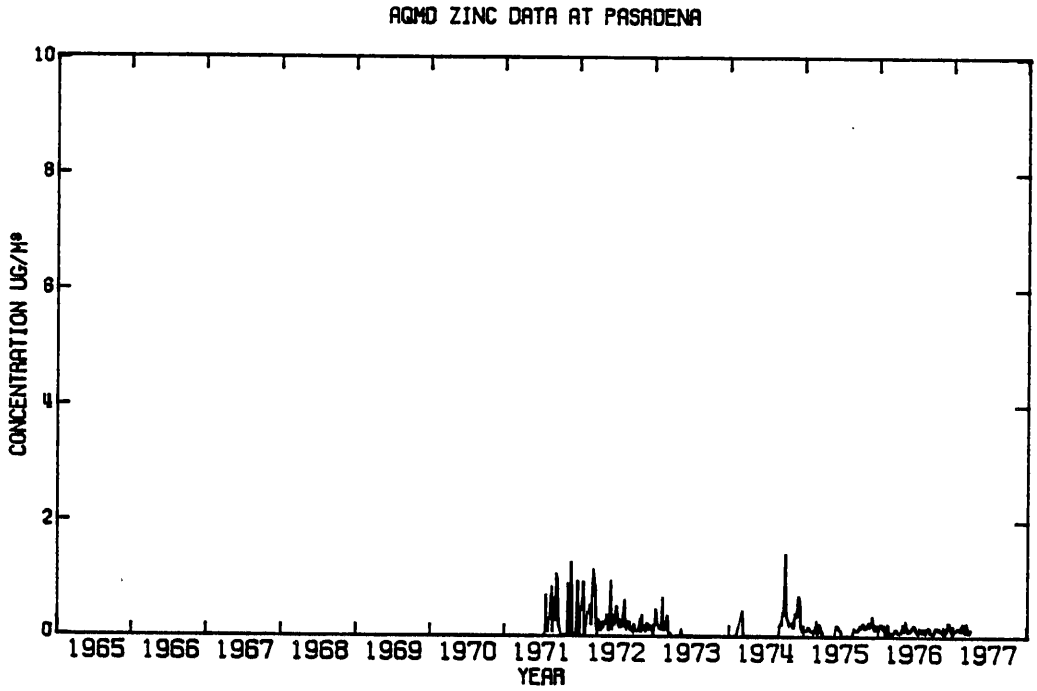



FIGURE A.7.13

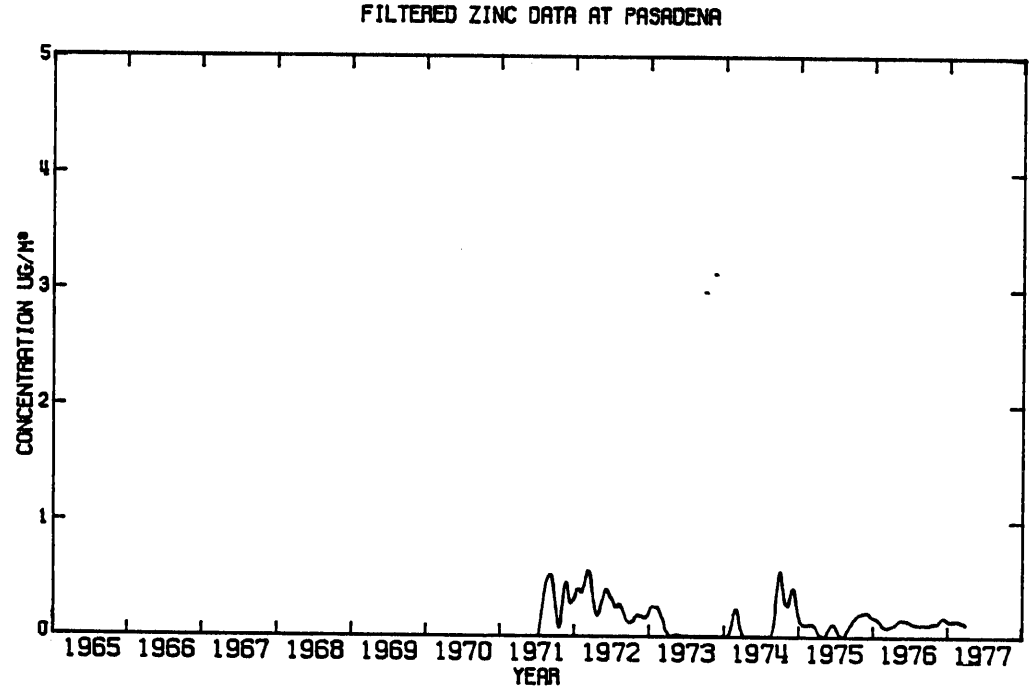



FIGURE A.7.14

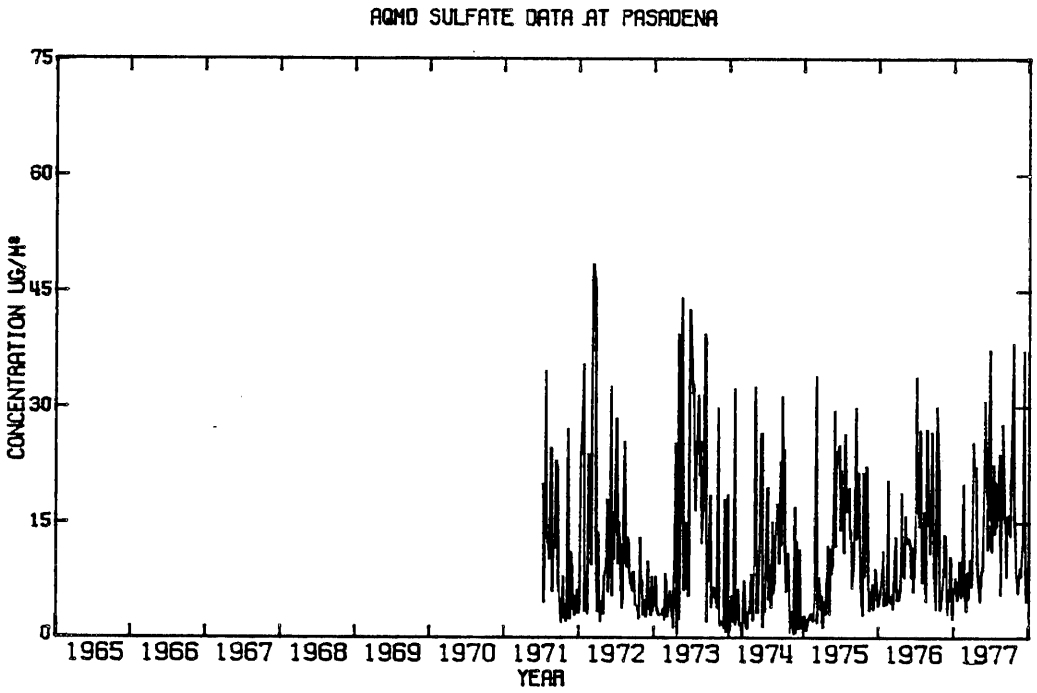



FIGURE A.7.15

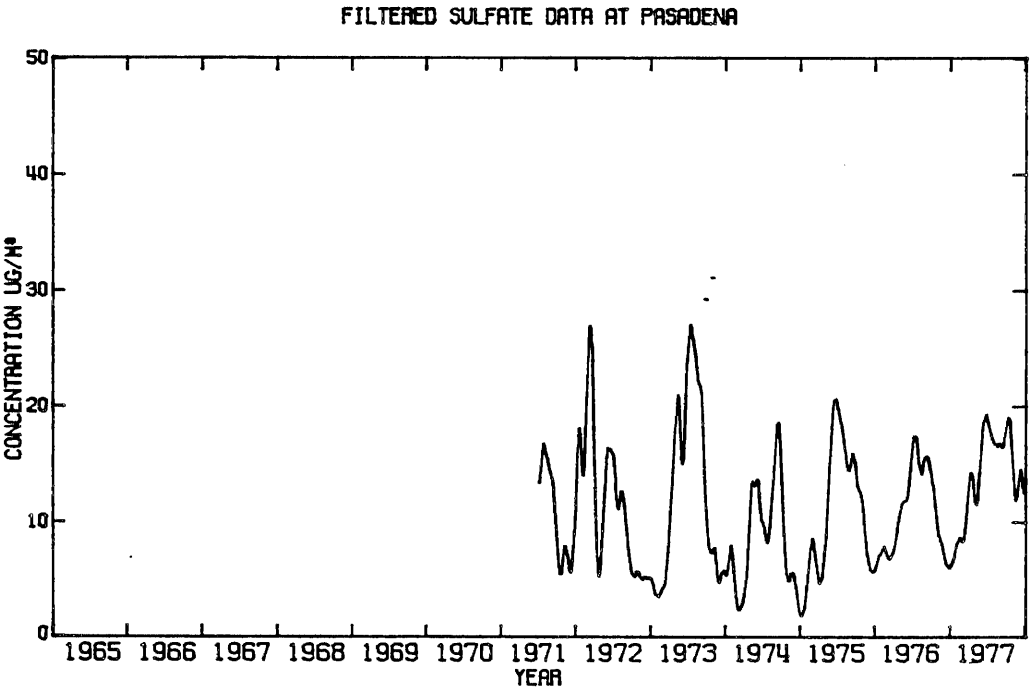



FIGURE A.7.16

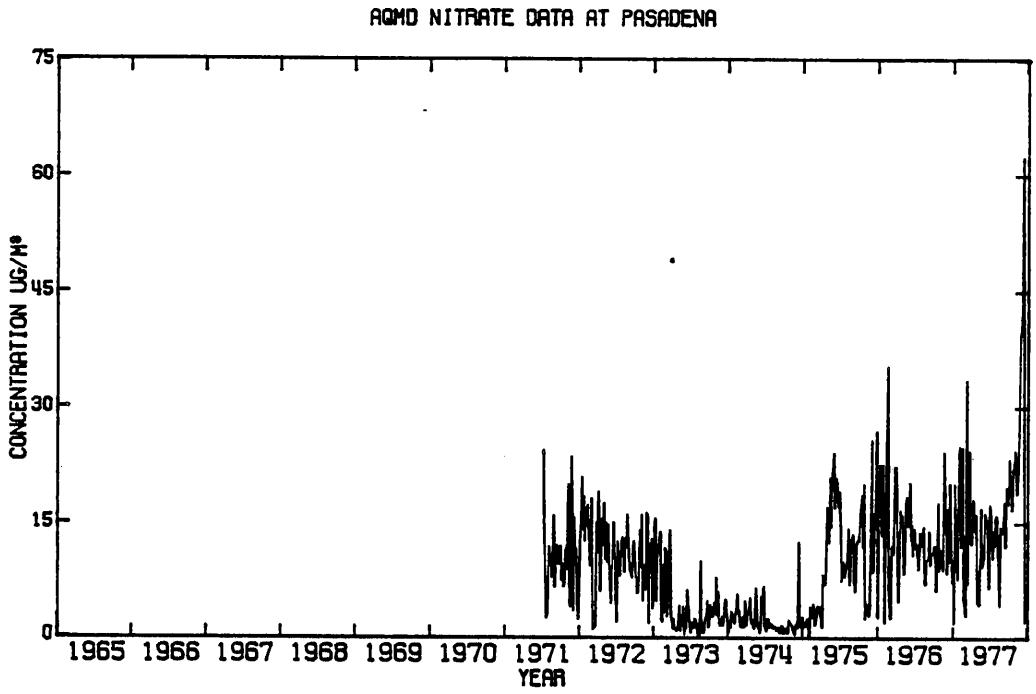



FIGURE A.7.17

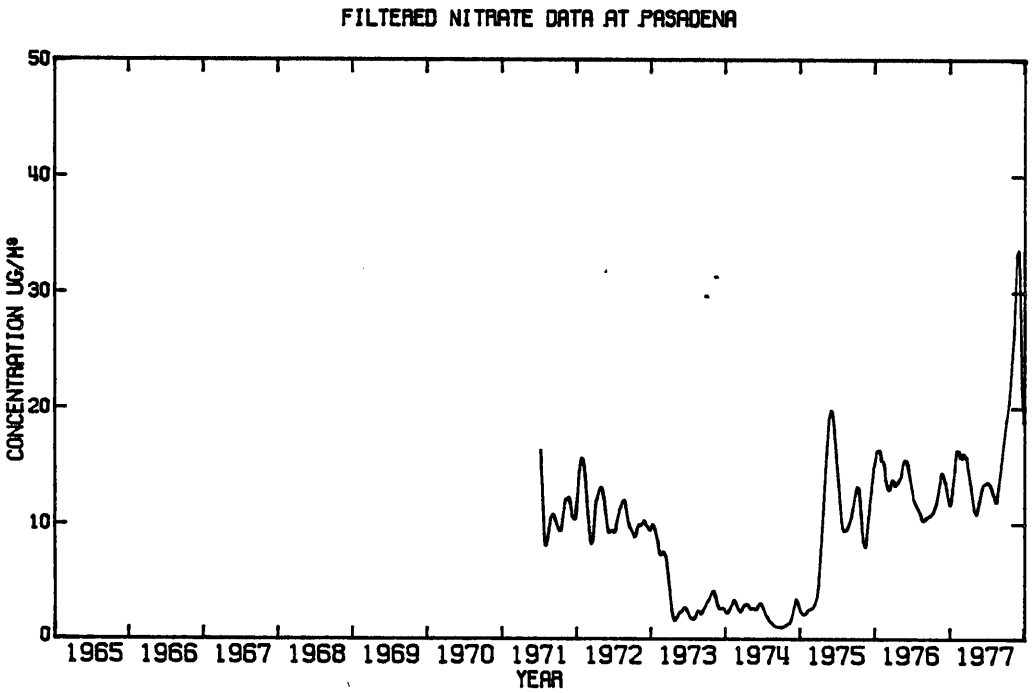



FIGURE A.7.18

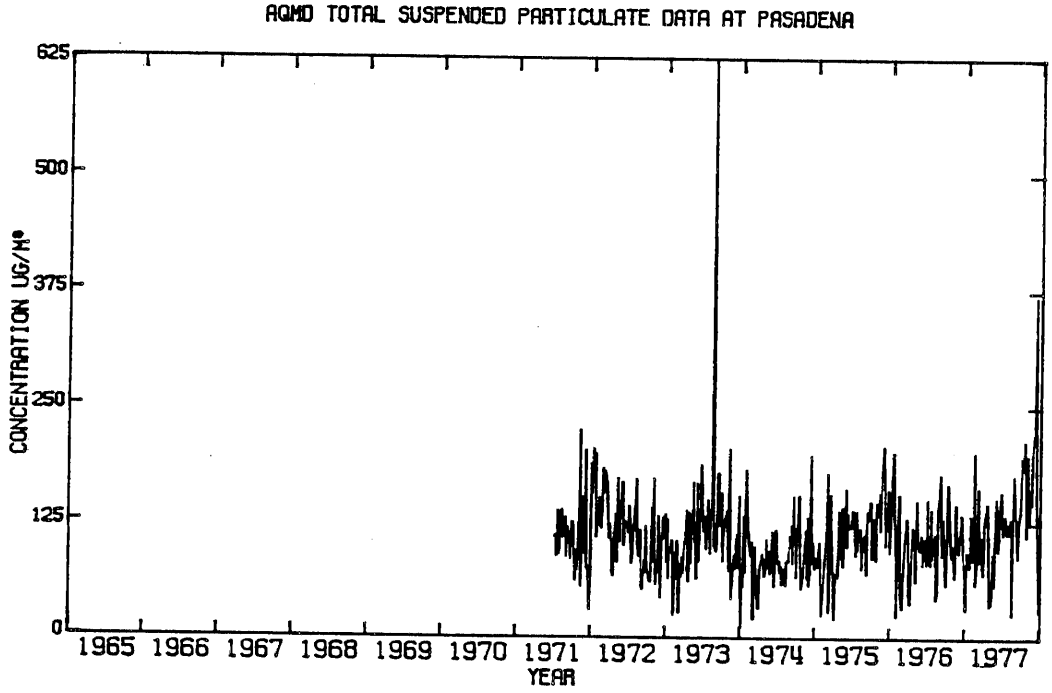



FIGURE A.7.19

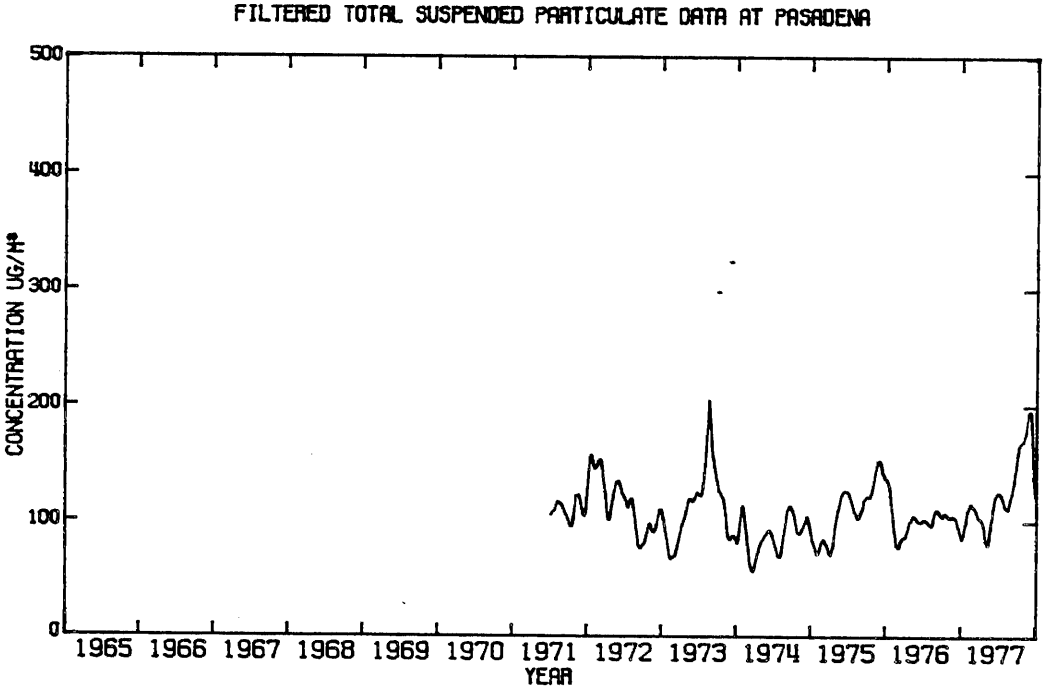



FIGURE A.7.20

## A.8 Monitoring Data at Reseda Site (SCAQMD)

TABLE A.8.1

Particulate Data Available at Reseda Monitoring Site (SCAQMD)

| Chemical Species | Figures[a] |
|---|---|
| Chromium | A.8.1 - A.8.2 |
| Copper | A.8.3 - A.8.4 |
| Iron | A.8.5 - A.8.6 |
| Lead | A.8.7 - A.8.8 |
| Manganese | A.8.9 - A.8.10 |
| Nickel | A.8.11 - A.8.12 |
| Zinc | A.8.13 - A.8.14 |
| Sulfates | A.8.15 - A.8.16 |
| Nitrates | A.8.17 - A.8.18 |
| Total Suspended Particulate | A.8.19 - A.8.20 |

a Odd numbered figures correspond to measured data and even numbered ones to filtered results.

TABLE A.8.2

Summary of Particulate Air Quality Statistics
at Reseda Monitoring Site (SCAQMD)
(Sep 1967 - Dec 1977)

| Chemical Species | Number of Samples | Statistics | | |
|---|---|---|---|---|
| | | Mean | Maximum | Minimum |
| | | (Micrograms $m^{-3}$) | | |
| Chromium | 587 | 0.011 | 0.19 | 0.00 |
| Copper | 584 | 0.15 | 1.62 | 0.00 |
| Iron | 574 | 2.29 | 18.93 | 0.00 |
| Lead | 614 | 3.32 | 16.12 | 0.12 |
| Manganese | 614 | 0.047 | 0.49 | 0.00 |
| Nickel | 583 | 0.019 | 0.20 | 0.00 |
| Zinc | 589 | 0.41 | 7.04 | 0.00 |
| Sulfates | 614 | 11.29 | 121.10 | 0.00 |
| Nitrates | 615 | 6.67 | 35.9 | 0.00 |
| TSP | 612 | 117.82 | 608.00 | 13.00 |

Note: All samples are 24 hour averages

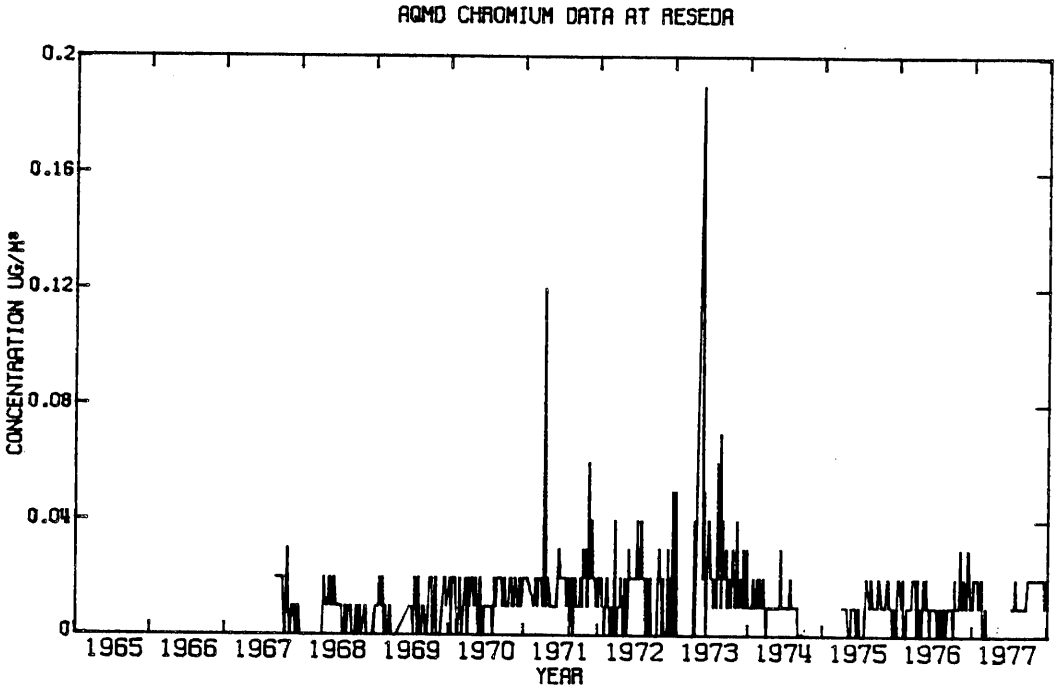



FIGURE A.8.1

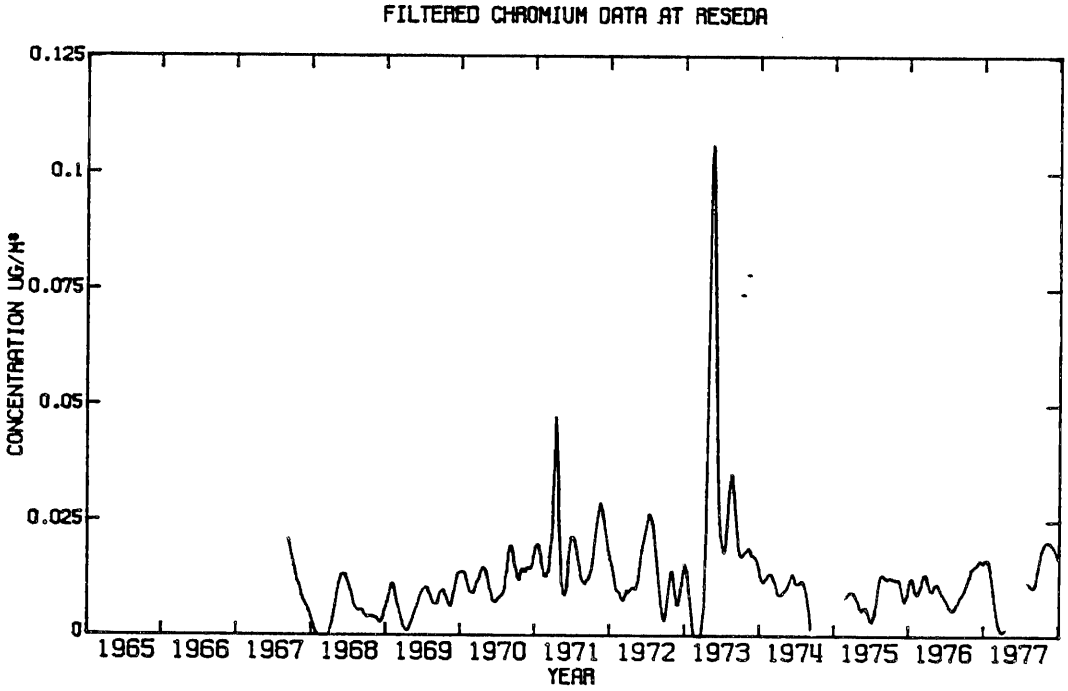



FIGURE A.8.2

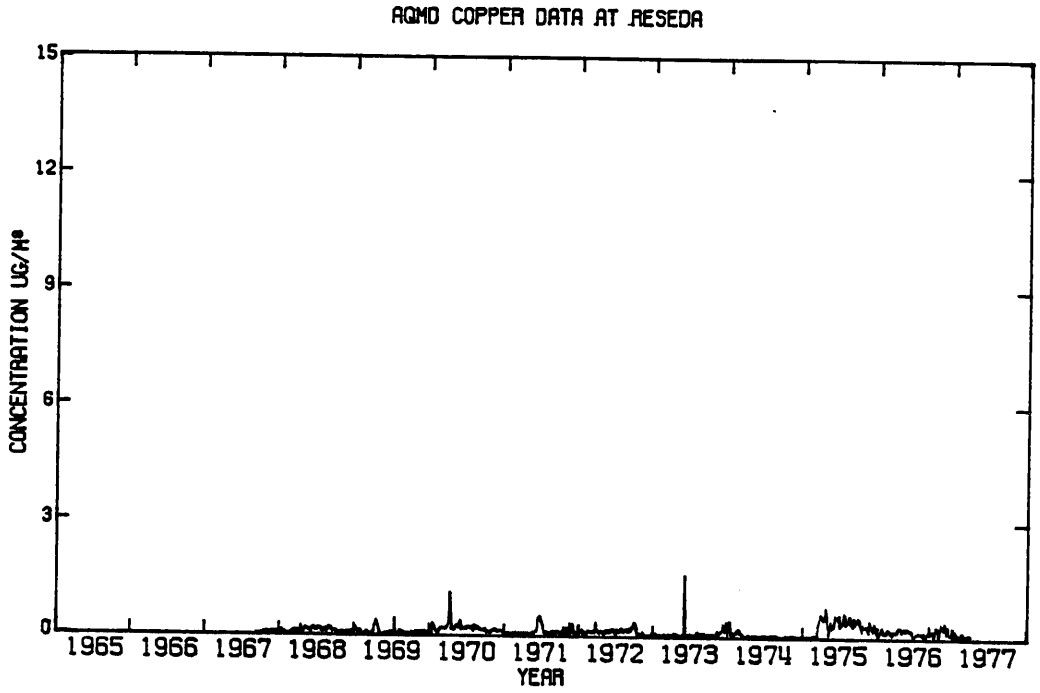



FIGURE A.8.3

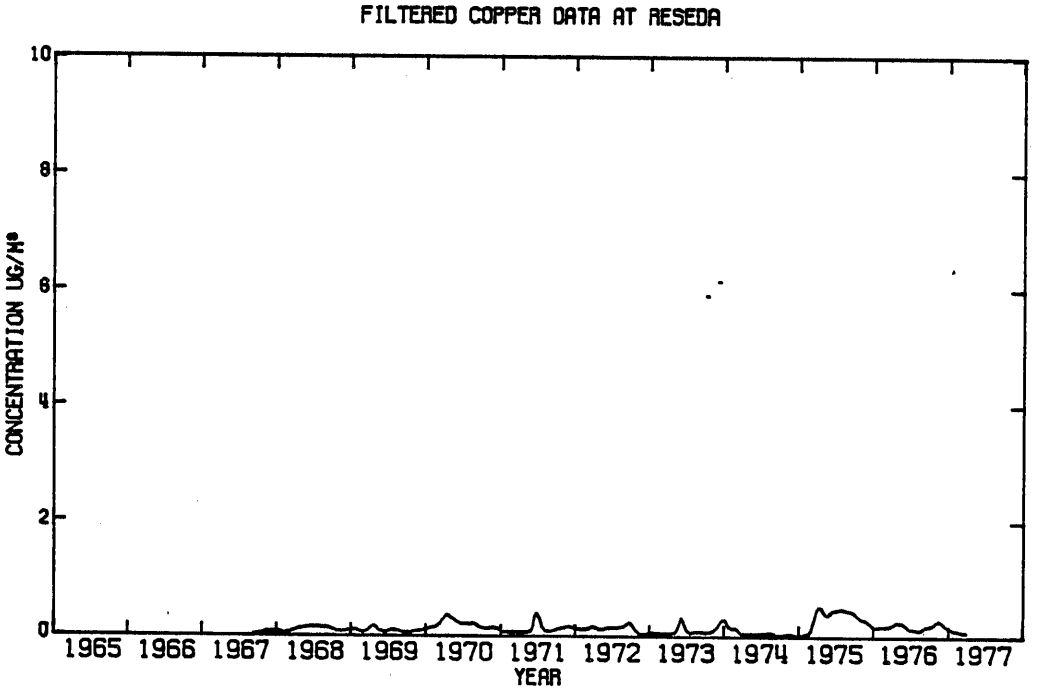



FIGURE A.8.4

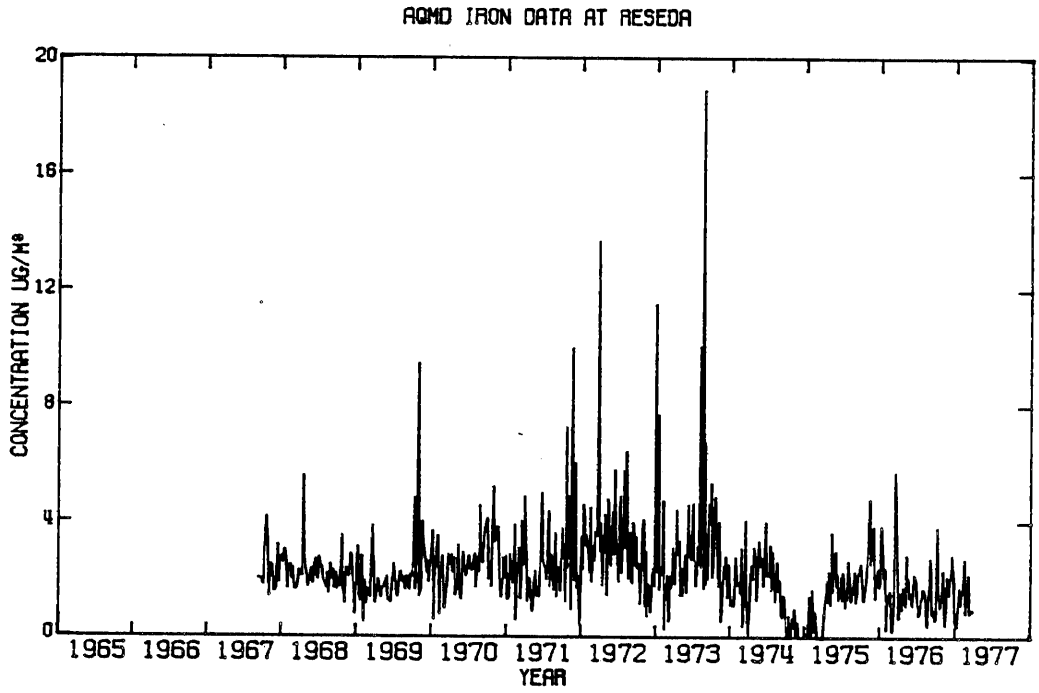



FIGURE A.8.5

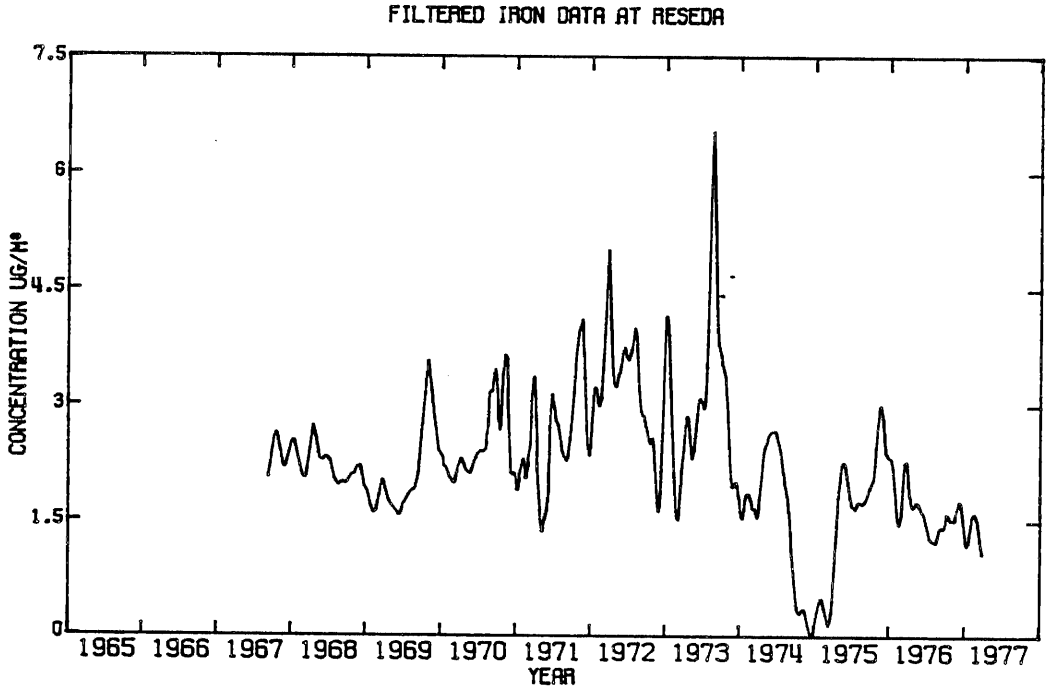



FIGURE A.8.6

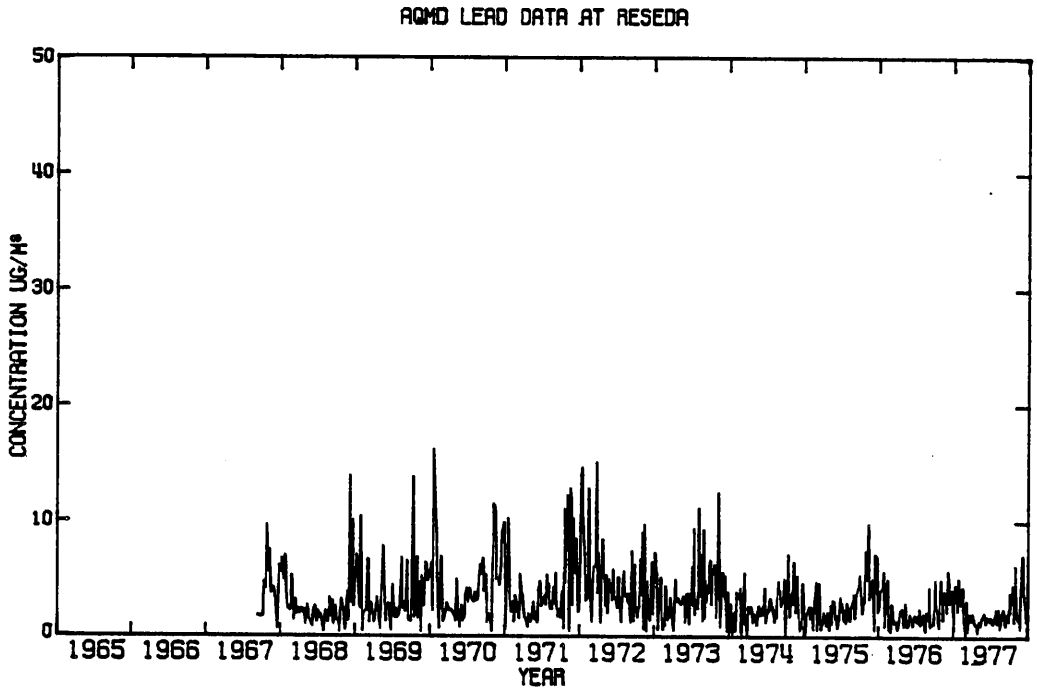



FIGURE A.8.7

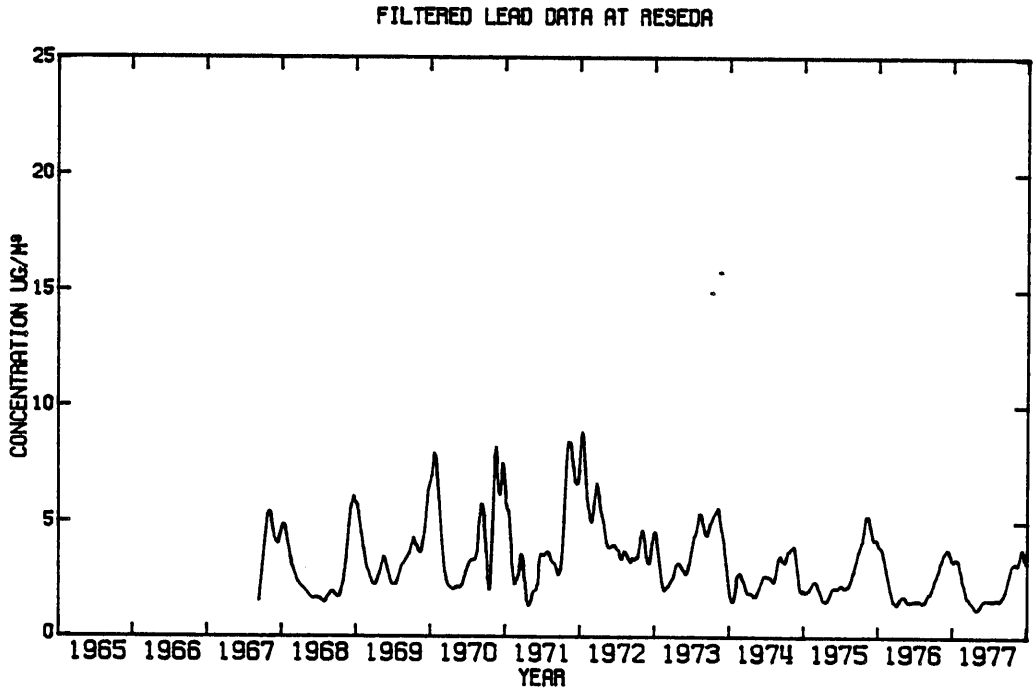



FIGURE A.8.8

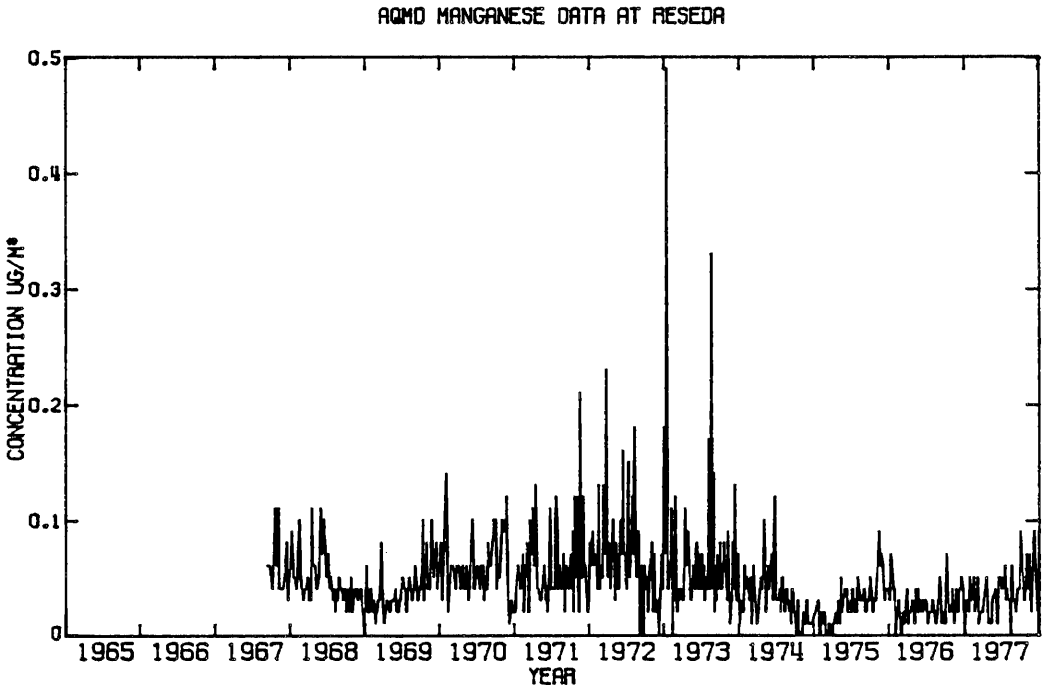



FIGURE A.8.9

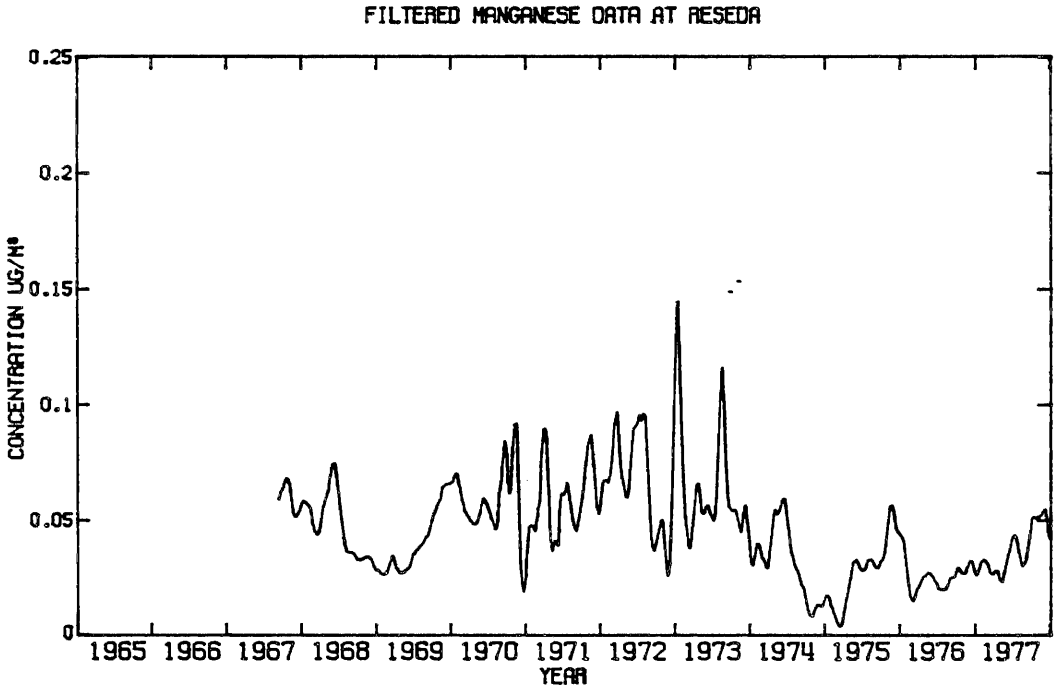



FIGURE A.8.10

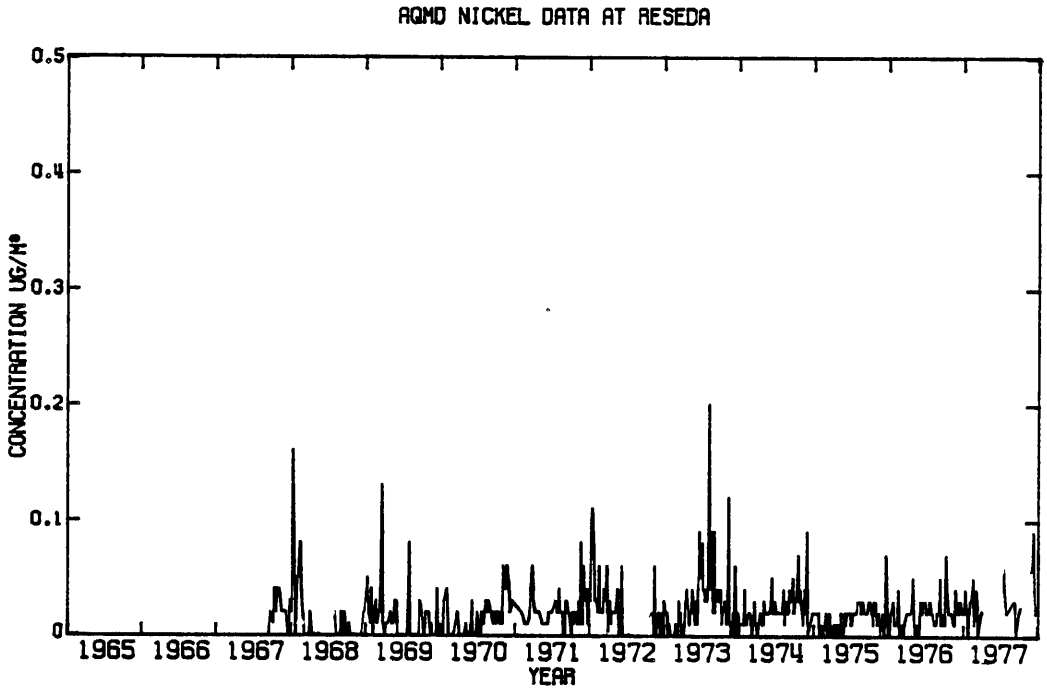



FIGURE A.8.11

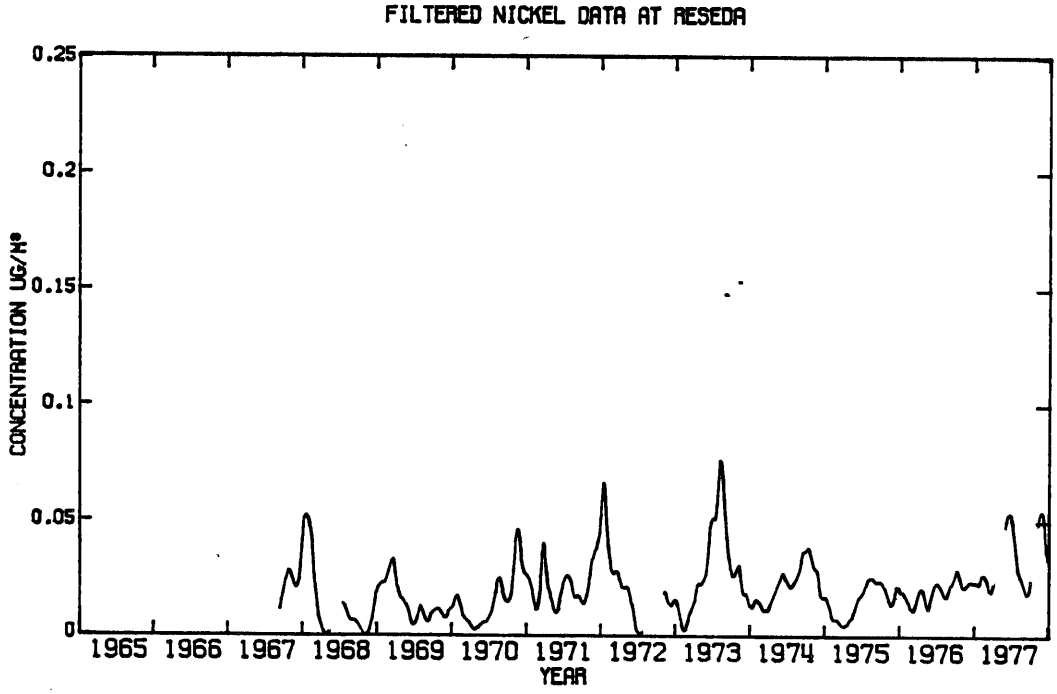



FIGURE A.8.12

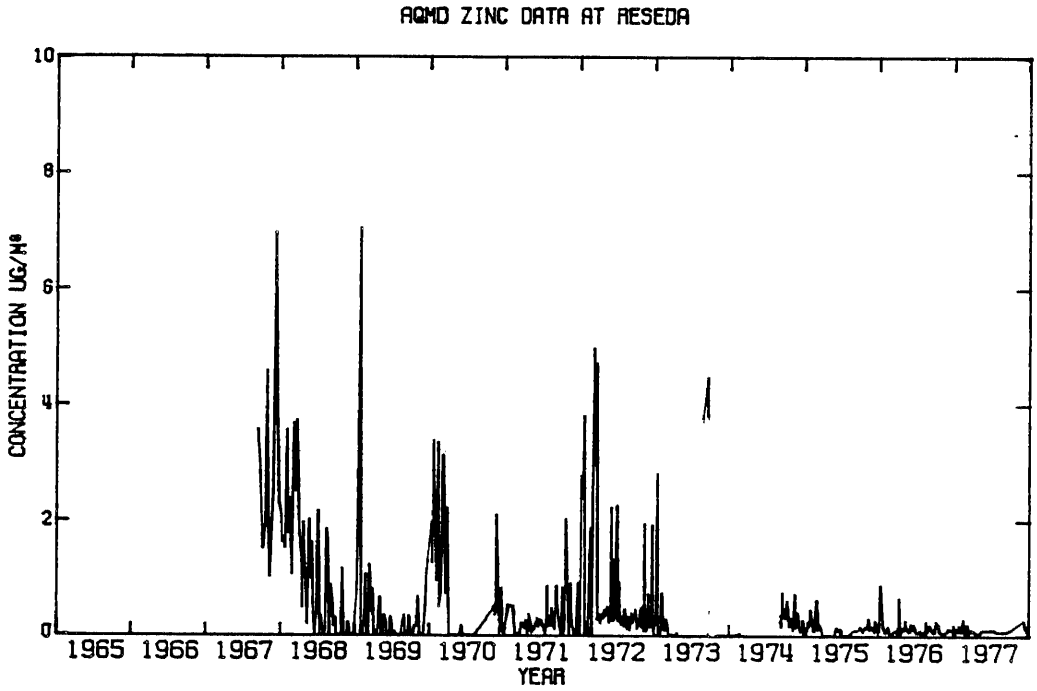



FIGURE A.8.13

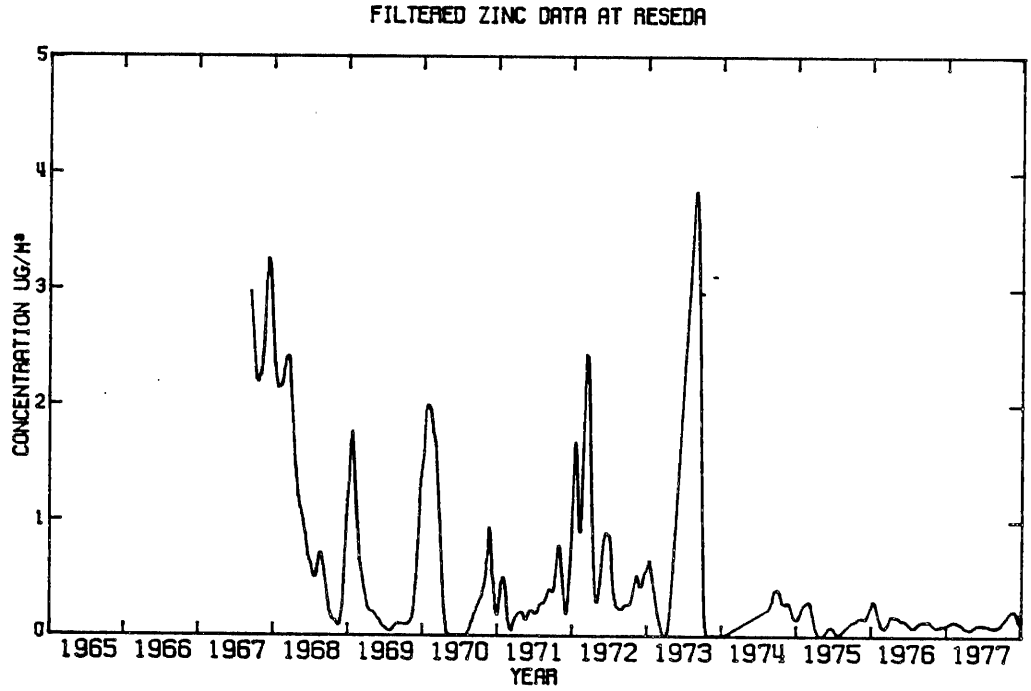



FIGURE A.8.14

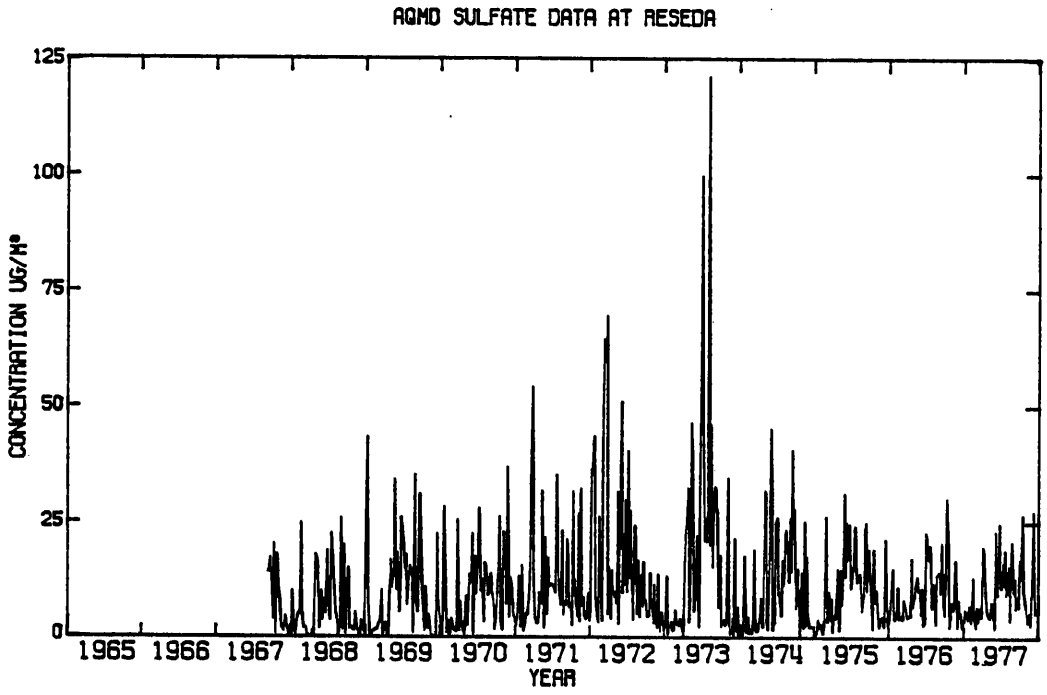



FIGURE A.8.15

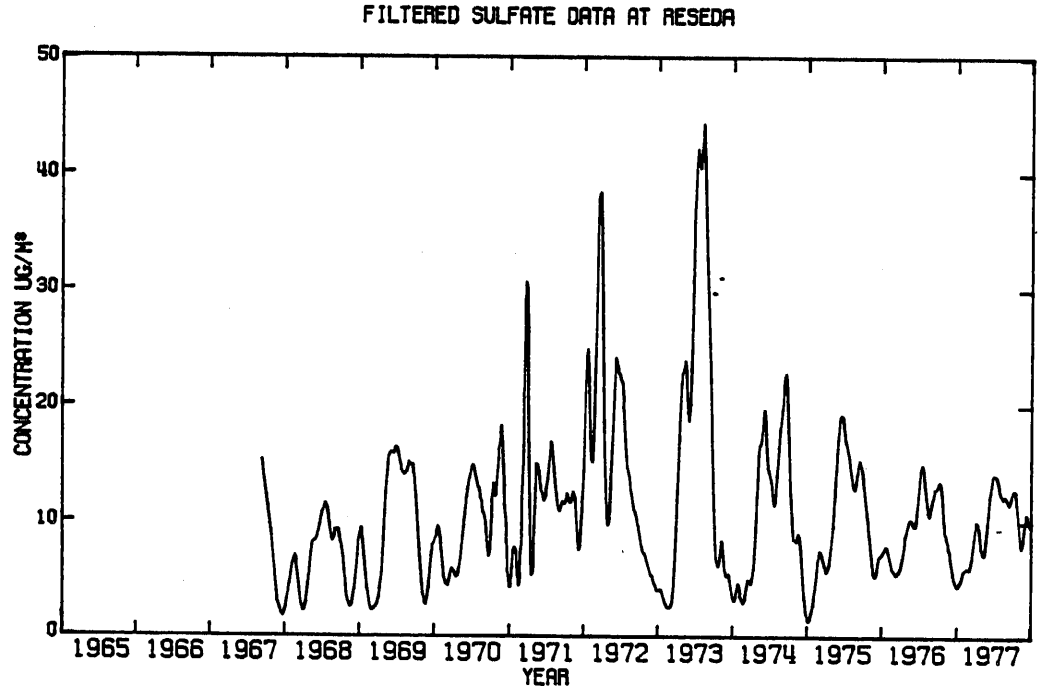



FIGURE A.8.16

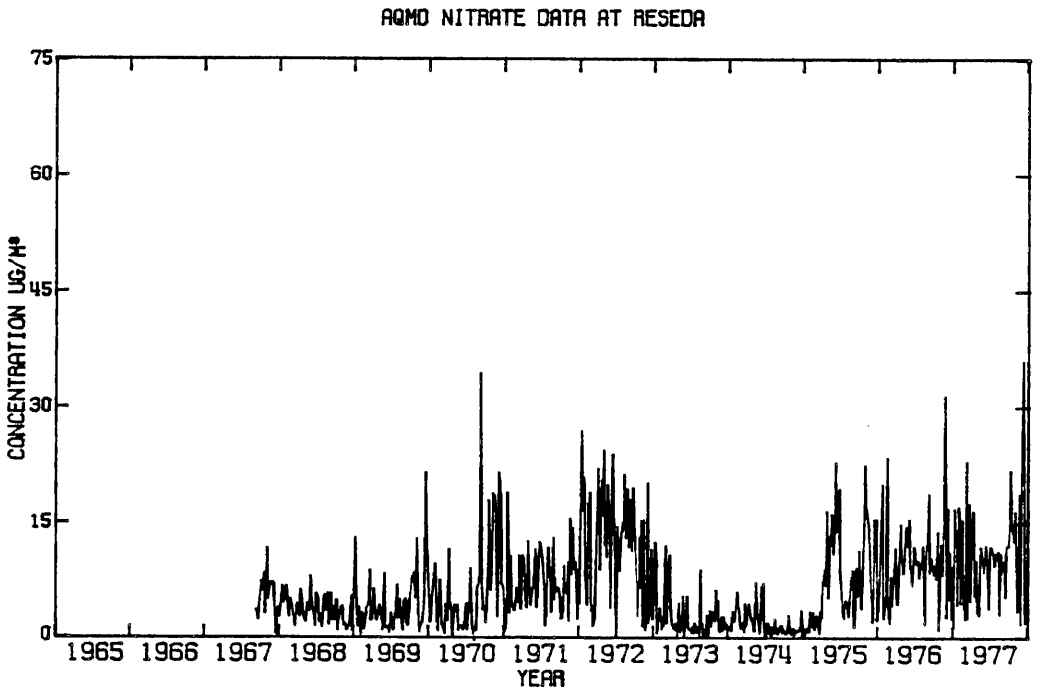



FIGURE A.8.17

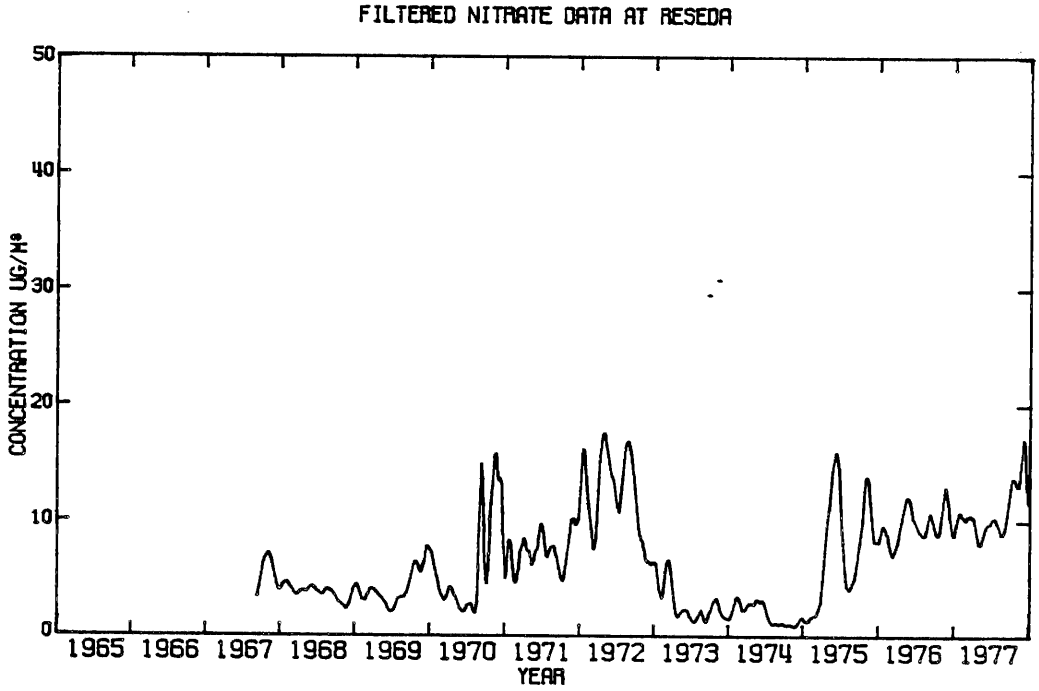



FIGURE A.8.18

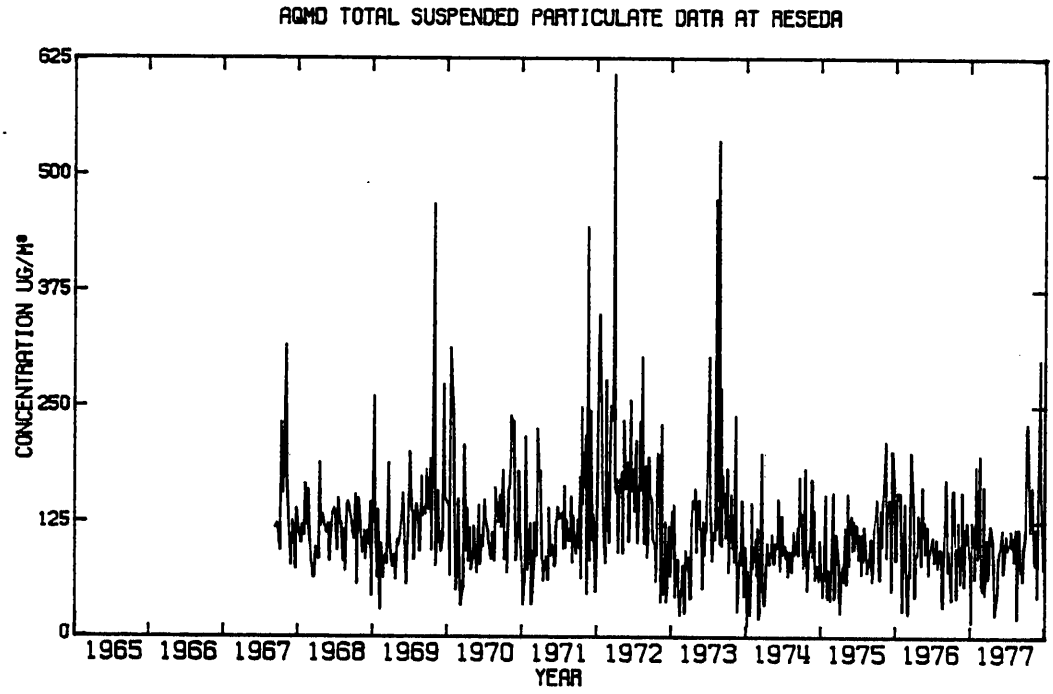



FIGURE A.8.19

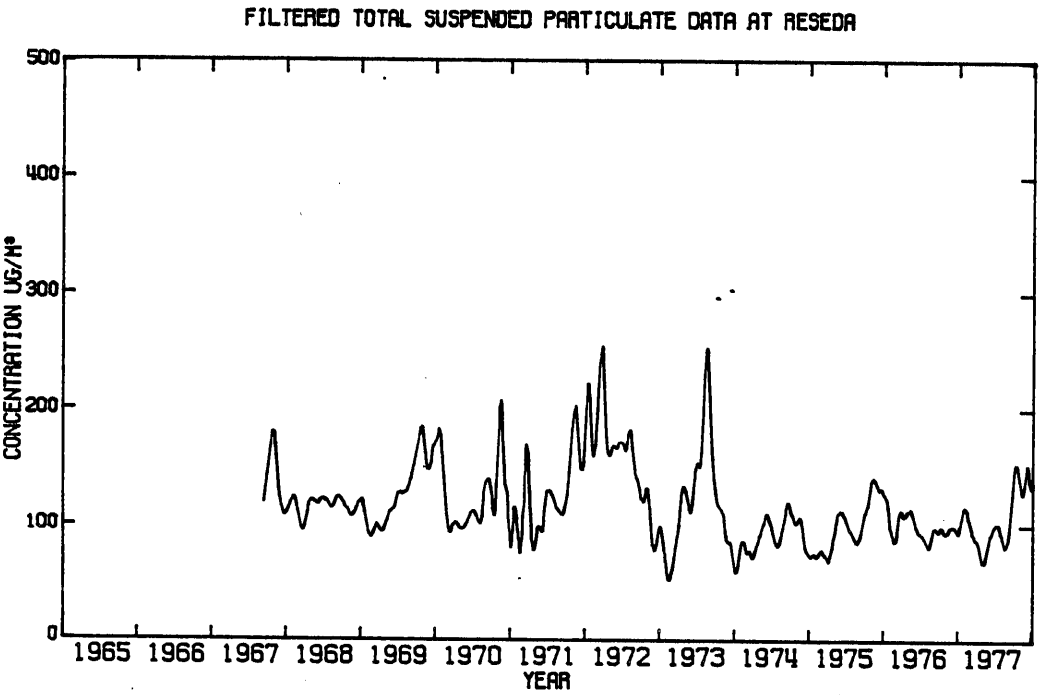



FIGURE A.8.20

## A.9 Monitoring Data at West Los Angeles Site (SCAQMD)

TABLE A.9.1

Particulate Data Available at West Los Angeles Monitoring Site (SCAQMD)

| Chemical Species | Figures[a] |
|---|---|
| Chromium | A.9.1 - A.9.2 |
| Copper | A.9.3 - A.9.4 |
| Iron | A.9.5 - A.9.6 |
| Lead | A.9.7 - A.9.8 |
| Manganese | A.9.9 - A.9.10 |
| Nickel | A.9.11 - A.9.12 |
| Zinc | A.9.13 - A.9.14 |
| Sulfates | A.9.15 - A.9.16 |
| Nitrates | A.9.17 - A.9.18 |
| Total Suspended Particulate | A.9.19 - A.9.20 |

a Odd numbered figures correspond to measured data and even numbered ones to filtered results.

TABLE A.9.2

Summary of Particulate Air Quality Statistics
at West Los Angeles Monitoring Site (SCAQMD)
(Aug 1965 - Dec 1977)

| Chemical Species | Number of Samples | Statistics | | |
|---|---|---|---|---|
| | | Mean | Maximum | Minimum |
| | | (Micrograms $m^{-3}$) | | |
| Chromium | 658 | 0.011 | 2.18 | 0.00 |
| Copper | 695 | 0.96 | 57.54 | 0.00 |
| Iron | 684 | 1.05 | 6.47 | 0.00 |
| Lead | 724 | 2.23 | 11.36 | 0.00 |
| Manganese | 726 | 0.024 | 0.81 | 0.00 |
| Nickel | 695 | 0.020 | 0.56 | 0.00 |
| Zinc | 661 | 0.48 | 12.95 | 0.00 |
| Sulfates | 733 | 8.60 | 46.10 | 0.00 |
| Nitrates | 731 | 5.90 | 32.60 | 0.00 |
| TSP | 733 | 84.82 | 310.00 | 23.00 |

Note: All samples are 24 hour averages

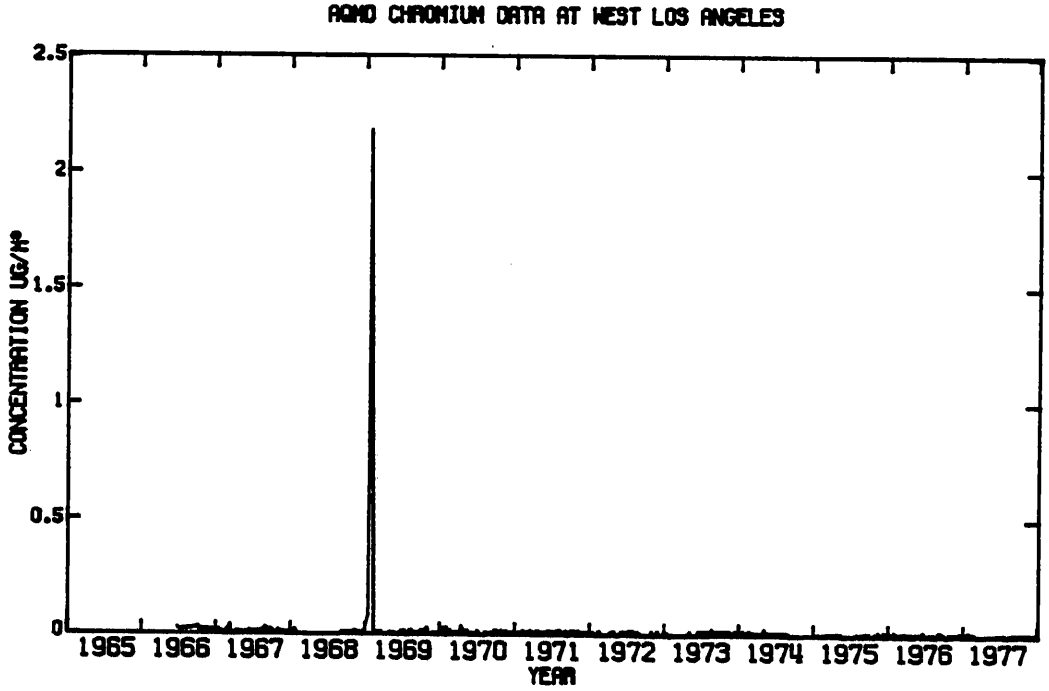



FIGURE A.9.1

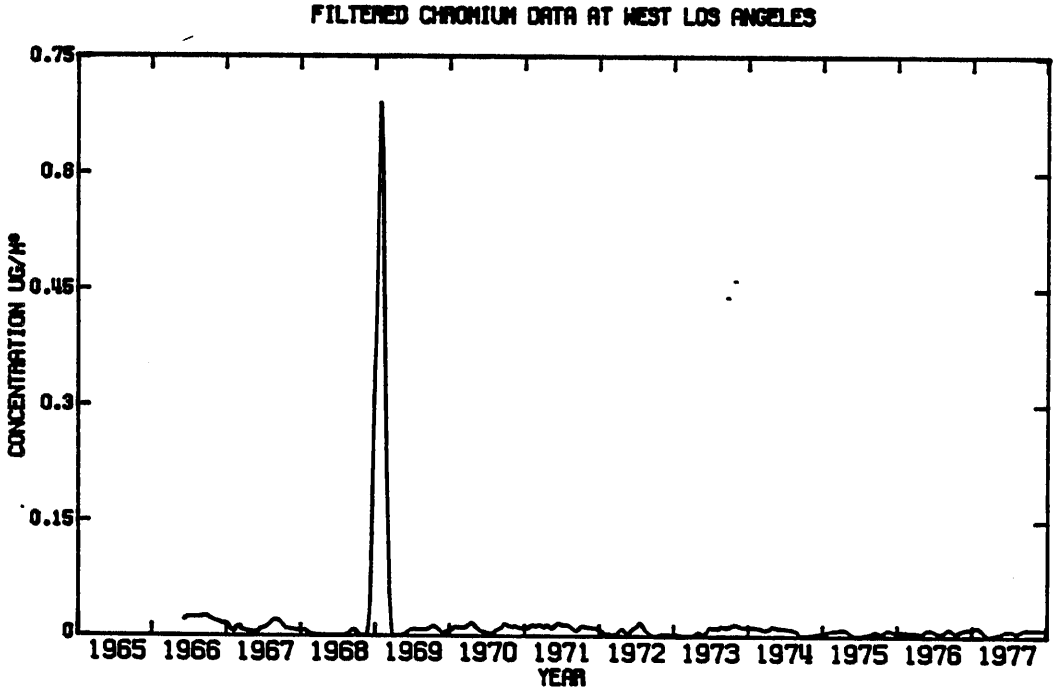



FIGURE A.9.2

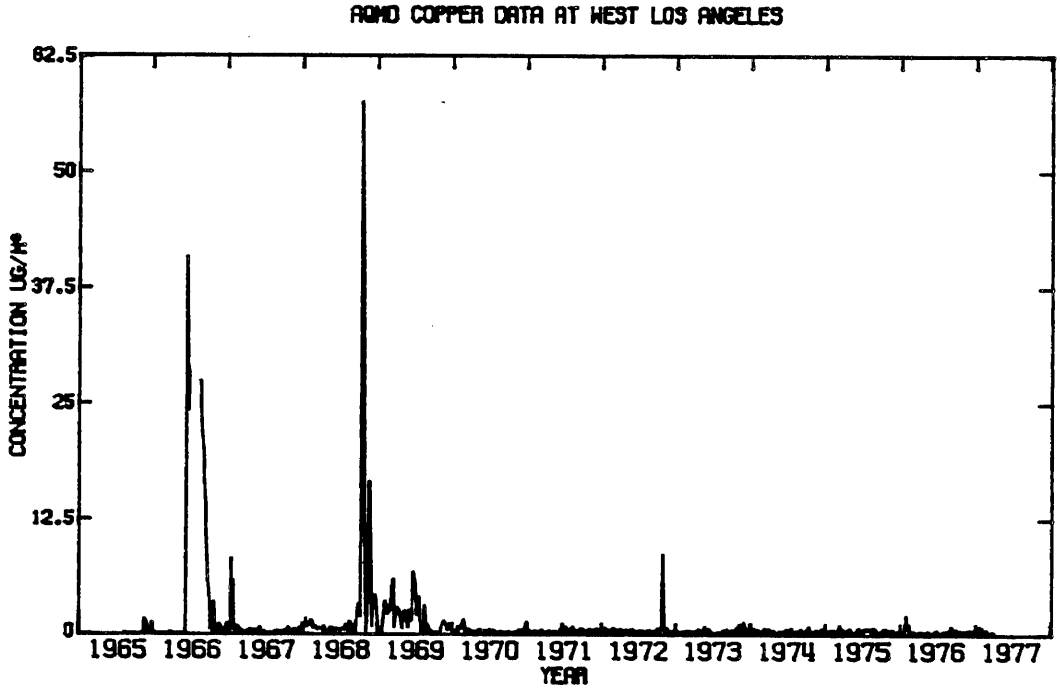



FIGURE A.9.3

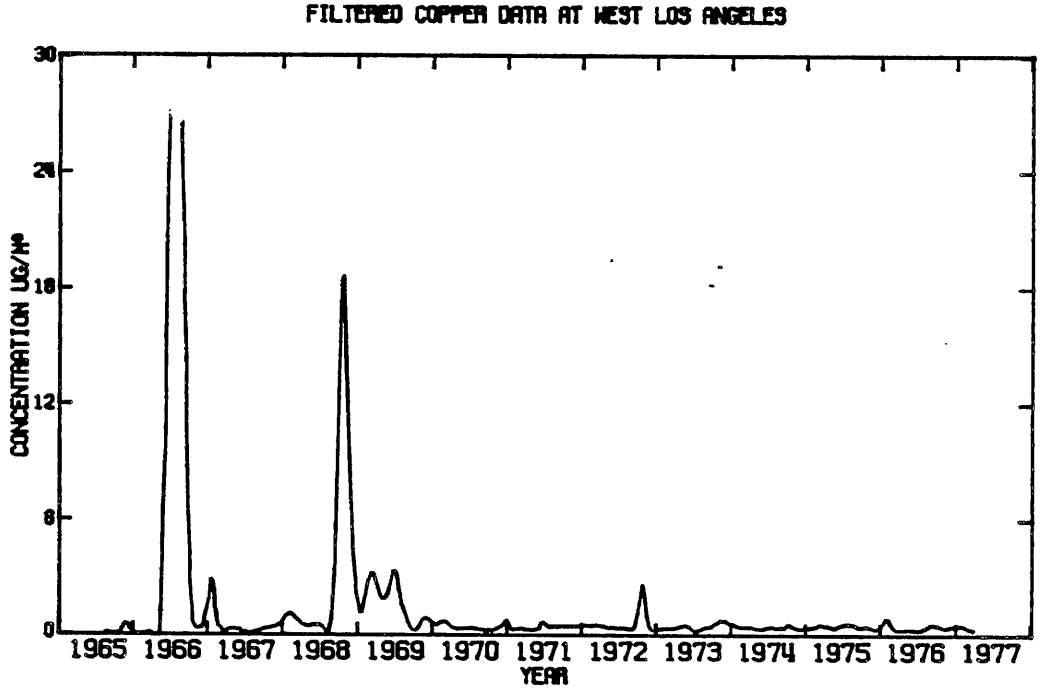



FIGURE A.9.4

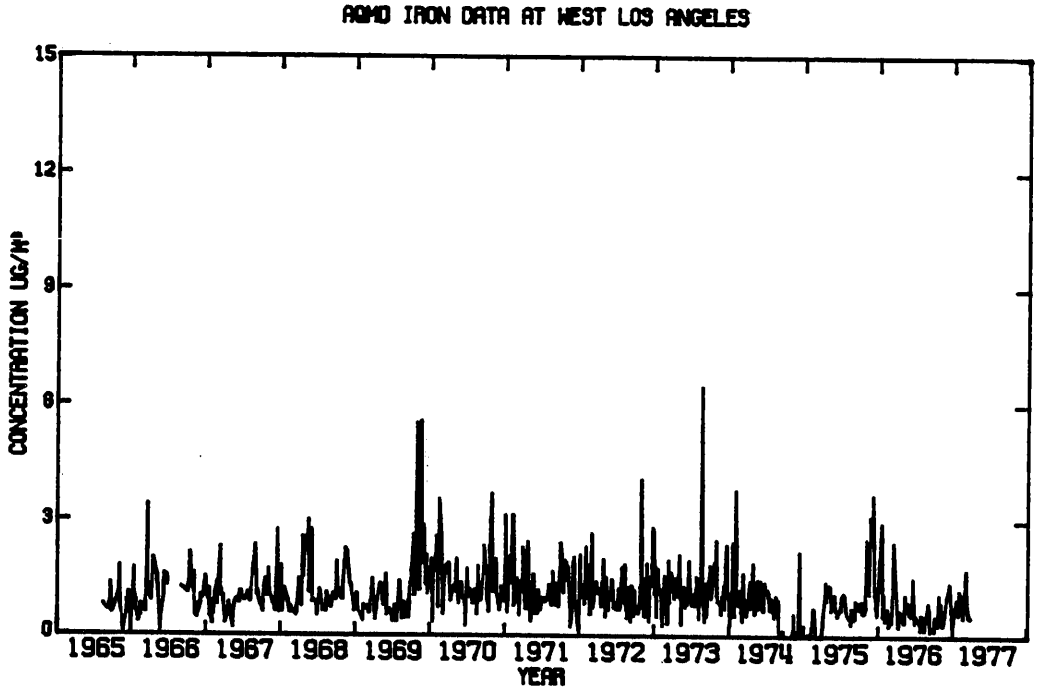



FIGURE A.9.5

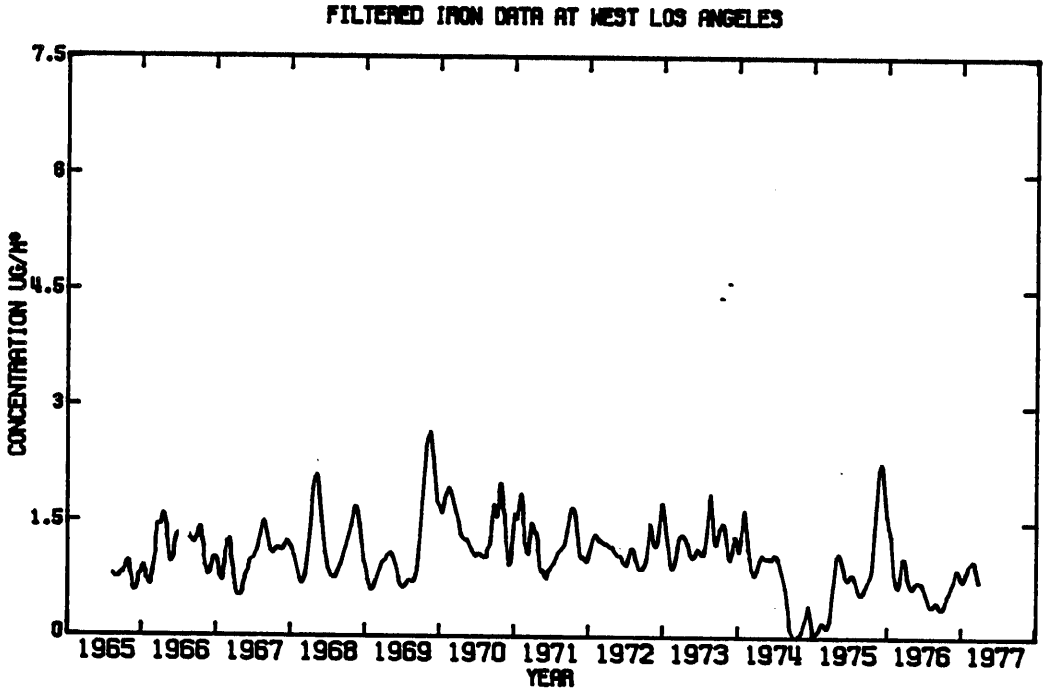



FIGURE A.9.6

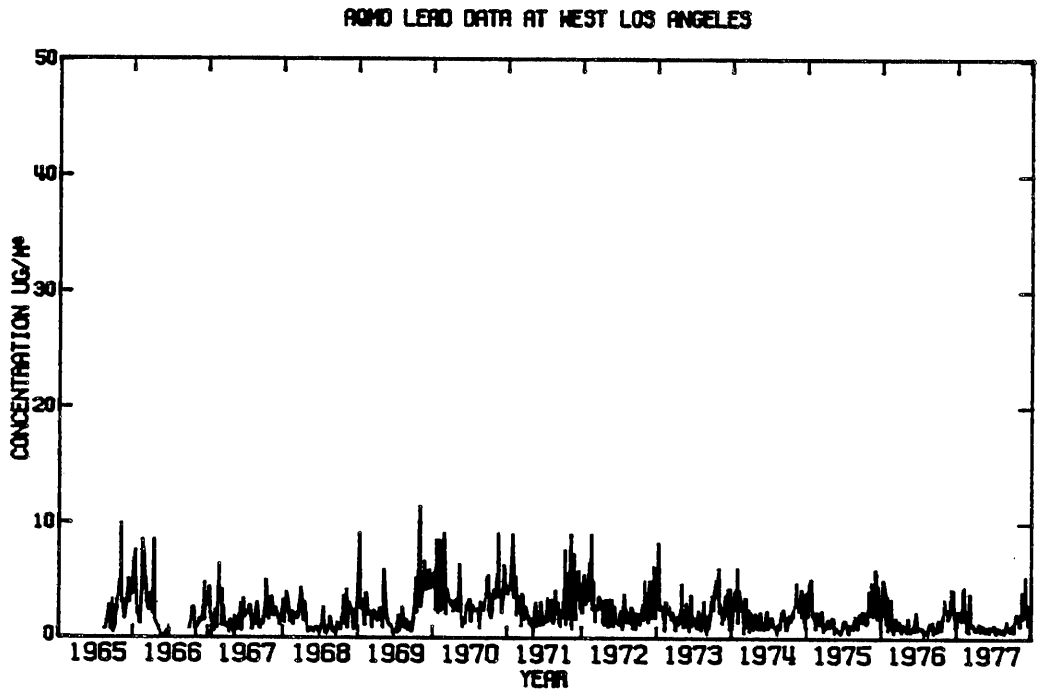



FIGURE A.9.7

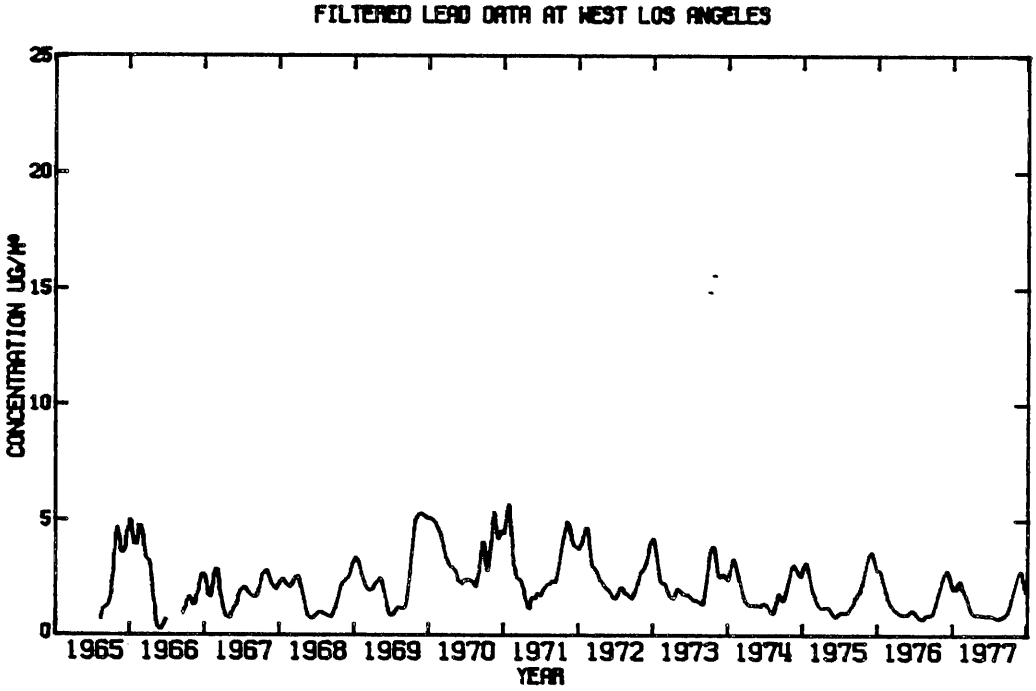



FIGURE A.9.8

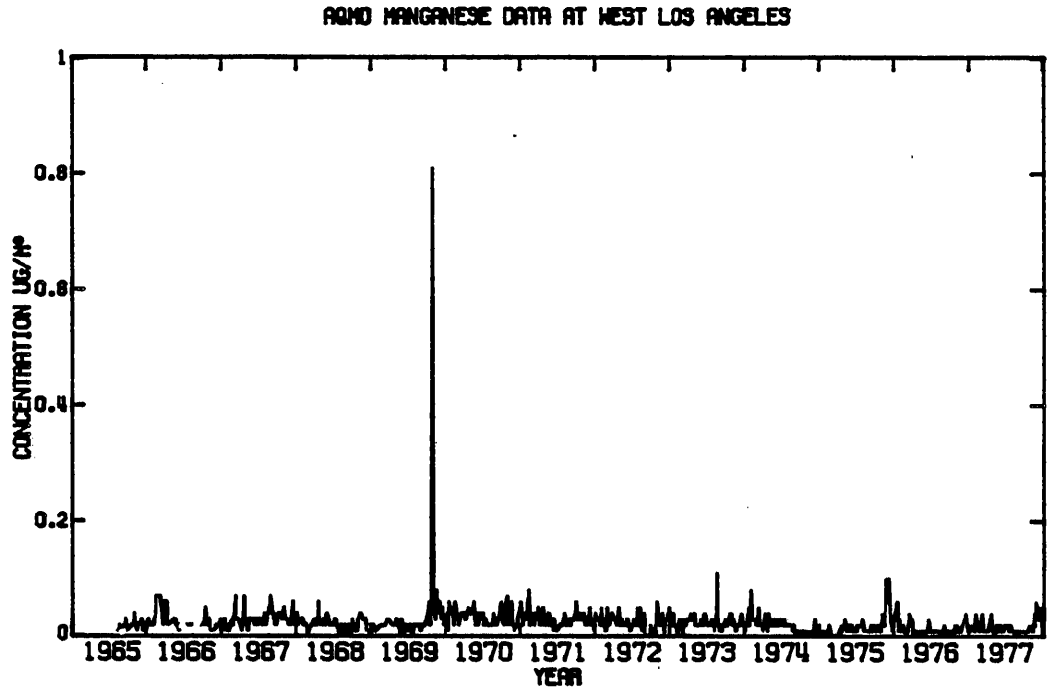



FIGURE A.9.9

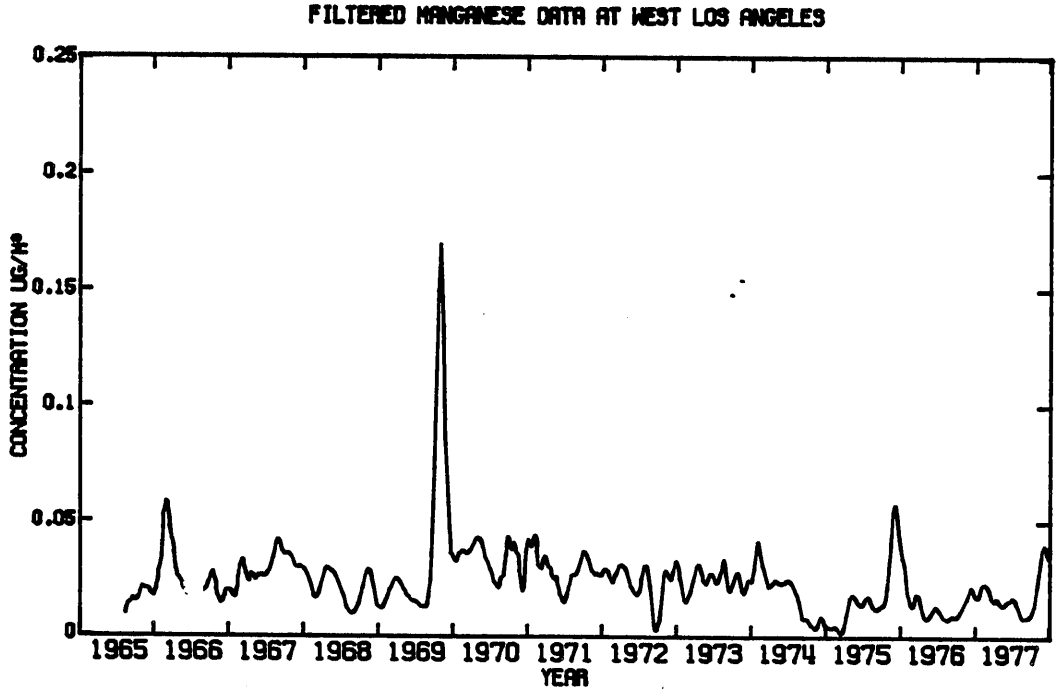



FIGURE A.9.10

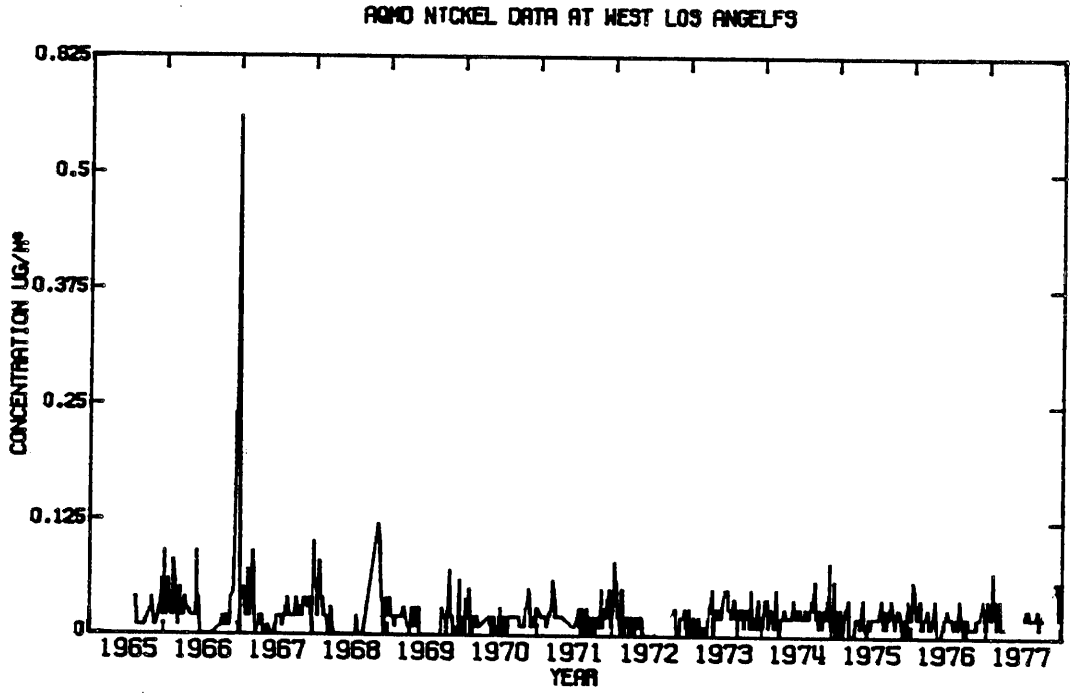



FIGURE A.9.11

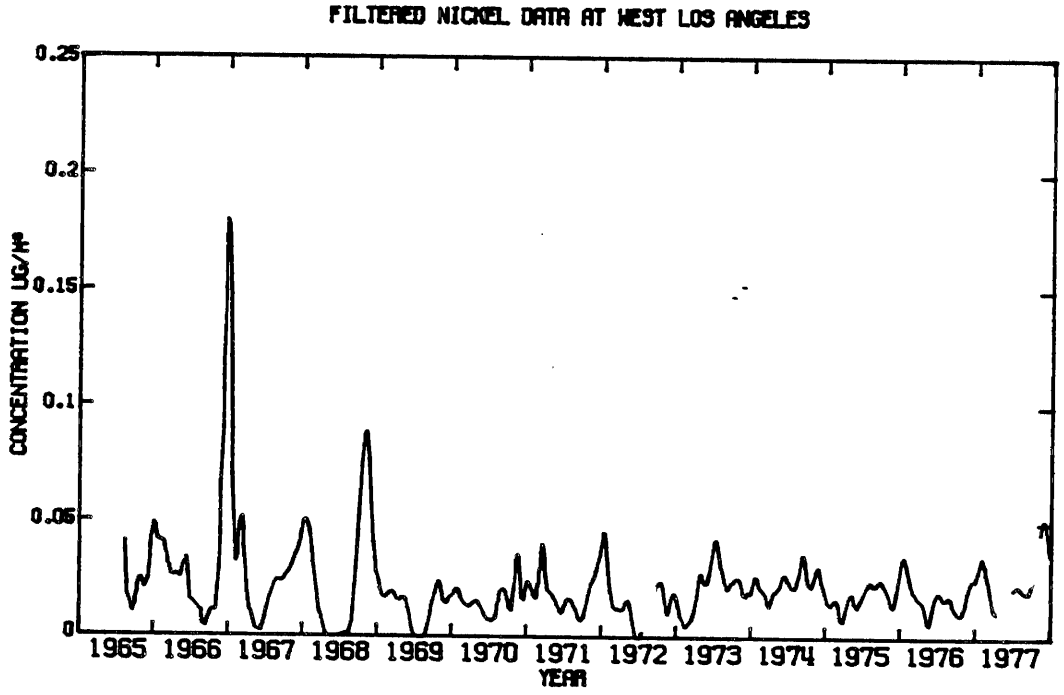



FIGURE A.9.12

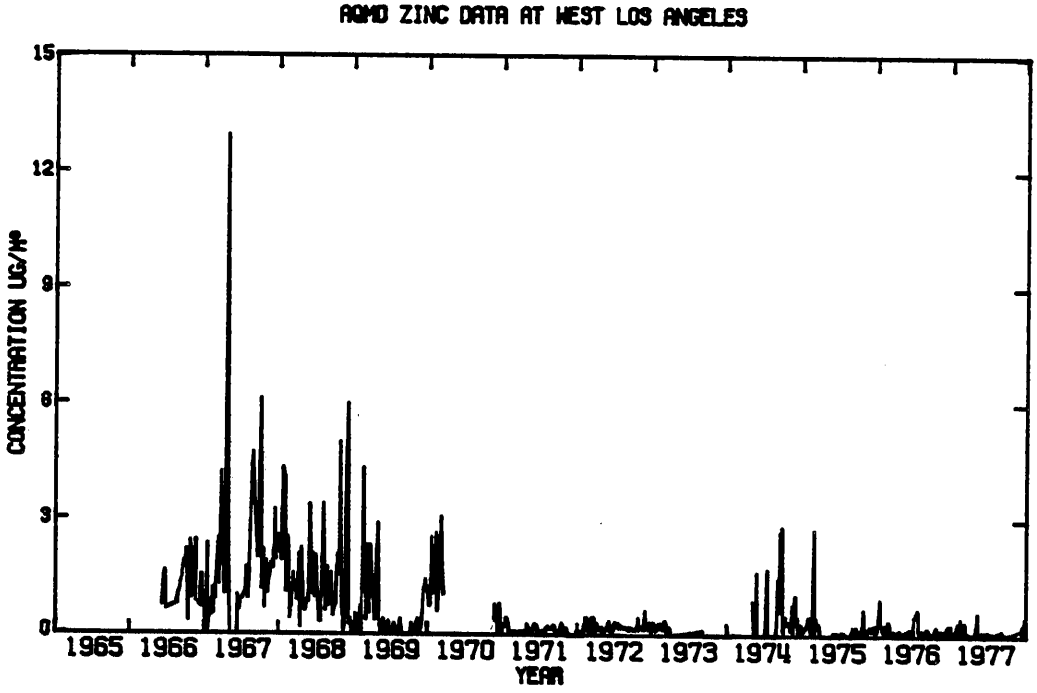



FIGURE A.9.13

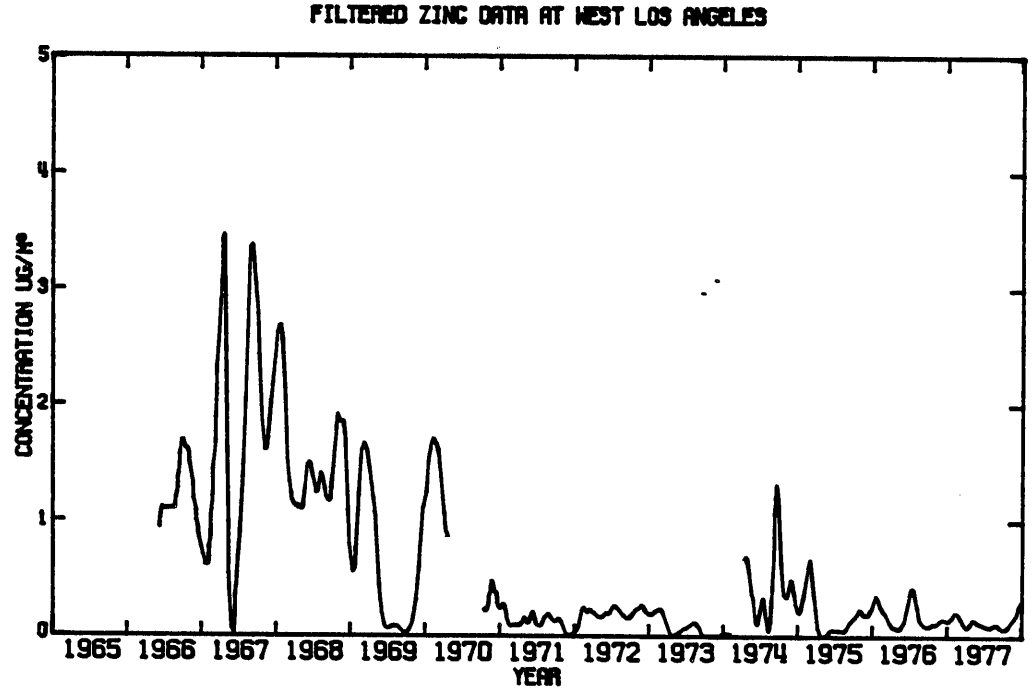



FIGURE A.9.14

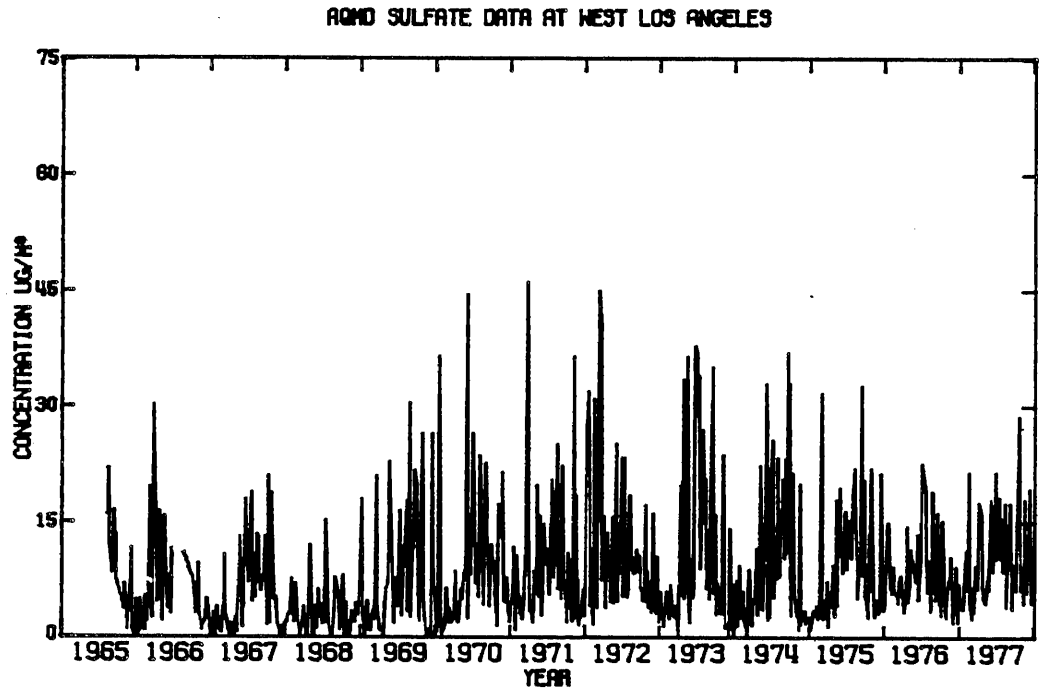



FIGURE A.9.15

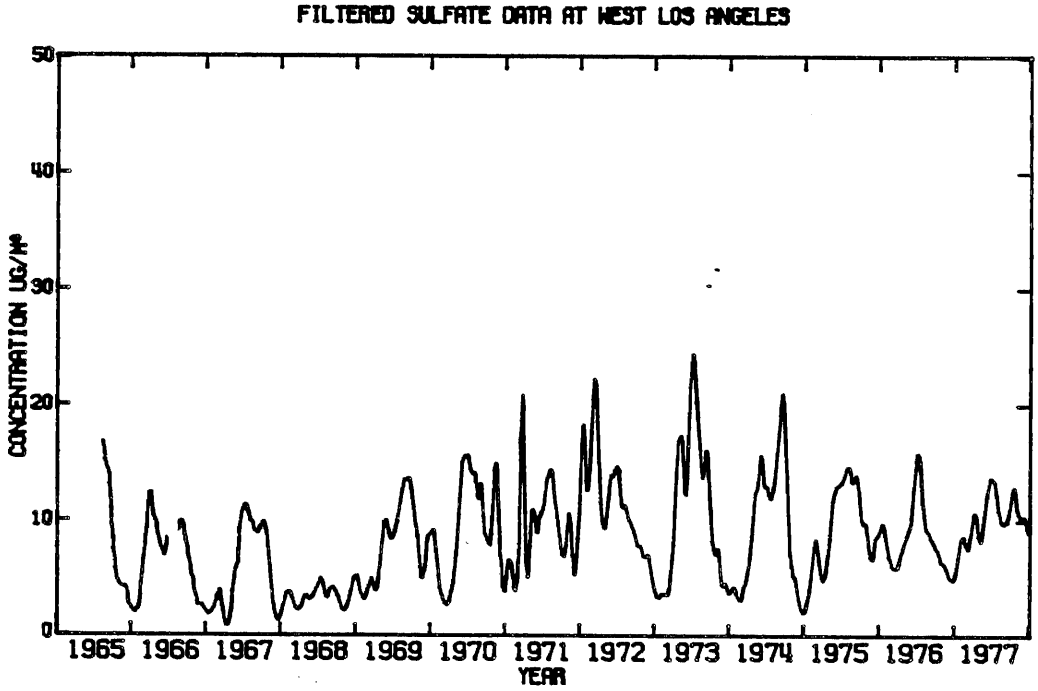



FIGURE A.9.16

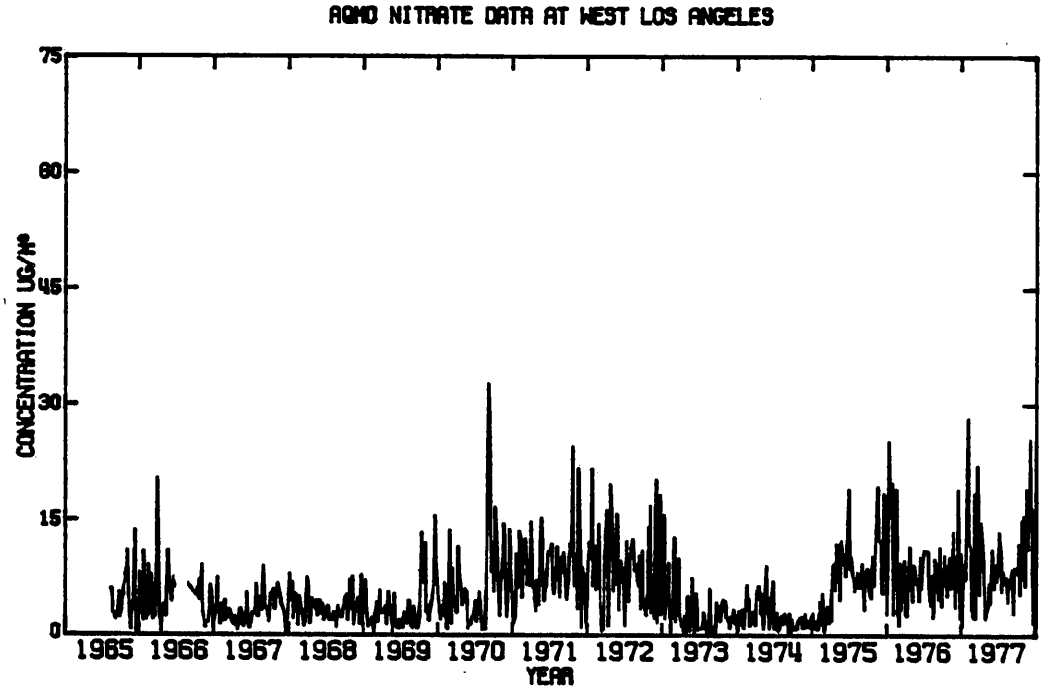



FIGURE A.9.17

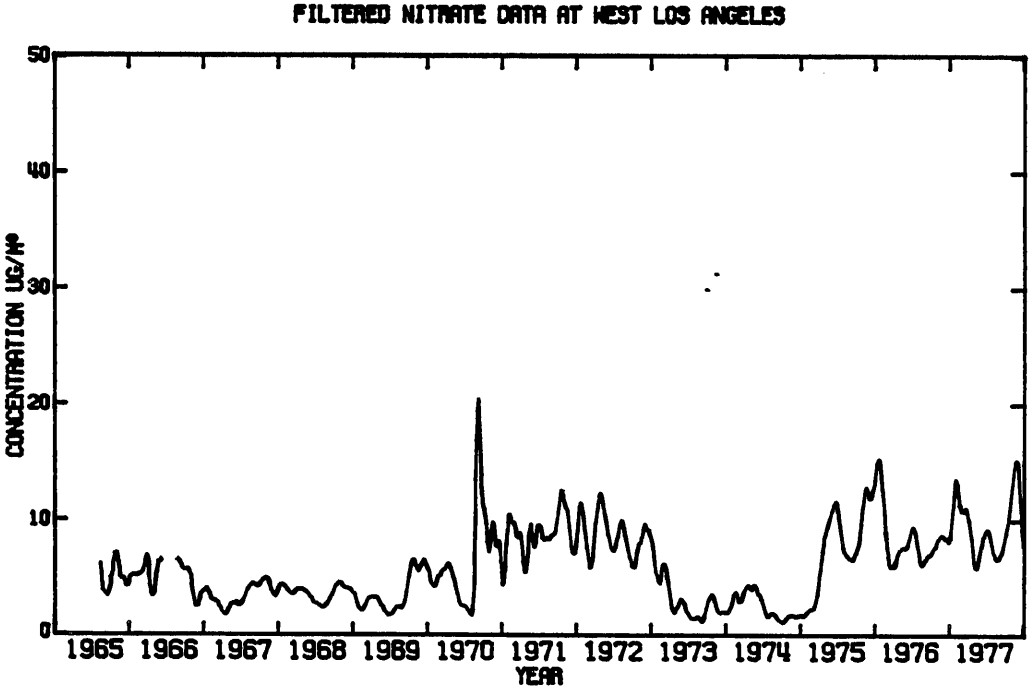



FIGURE A.9.18

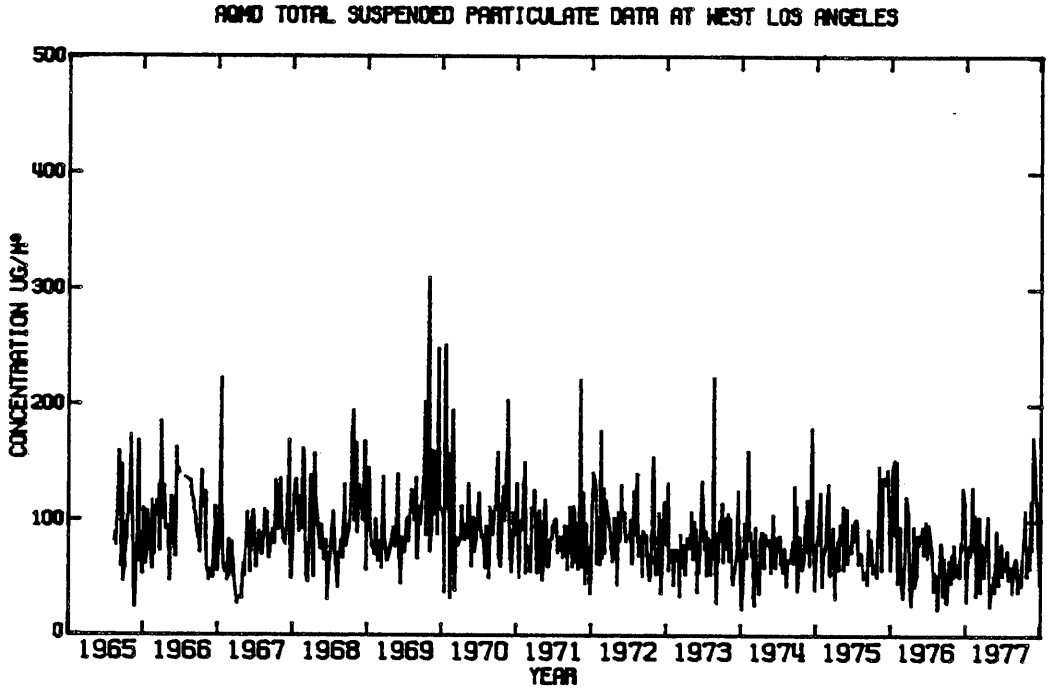



FIGURE A.9.19

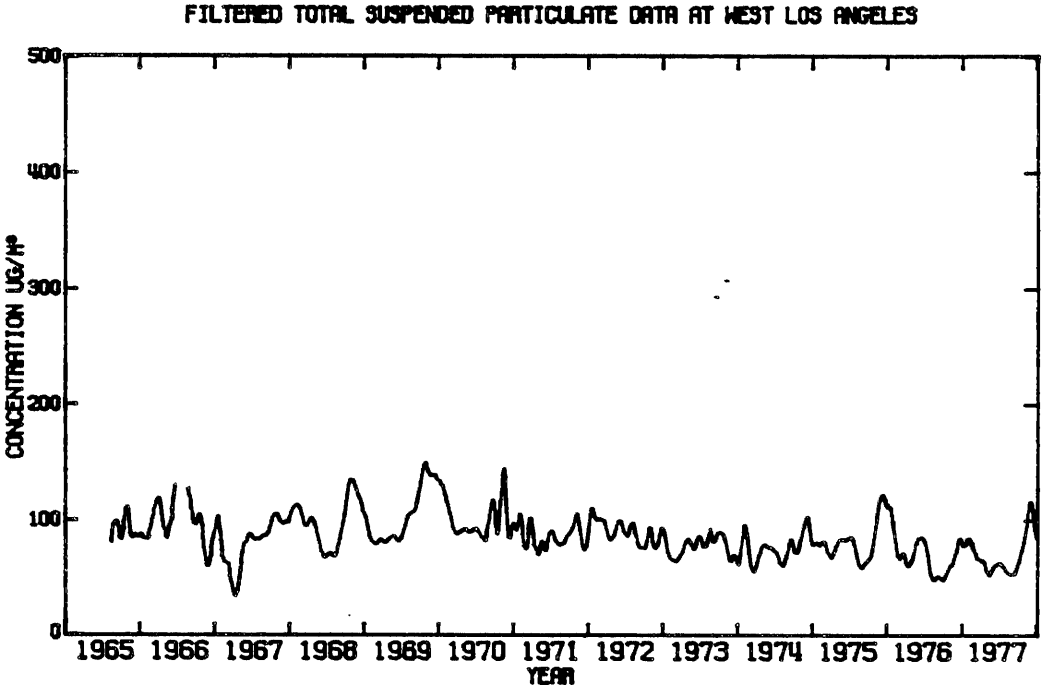



FIGURE A.9.20

## A.10 Monitoring Data at Anaheim Site (NASN)

TABLE A.10.1

Particulate Data Available for Anaheim Monitoring Site (NASN)

| Particulate Measurement | Figure |
|---|---|
| Cadmium | A.10.1 |
| Chromium | A.10.2 |
| Cobalt | A.10.3 |
| Copper | A.10.4 |
| Iron | A.10.5 |
| Lead | A.10.6 |
| Manganese | A.10.7 |
| Tin | A.10.8 |
| Titanium | A.10.9 |
| Vanadium | A.10.10 |
| Sulfates | A.10.11 |
| Nitrates | A.10.12 |
| Ammonium Ion | A.10.13 |
| Total Suspended Particulate | A.10.14 |

TABLE A.10.2

Summary of Particulate Air Quality Statistics
at Anaheim Monitoring Site (NASN)
(1969 - 1976)

| Chemical Species | Number of Samples | Statistics | | |
|---|---|---|---|---|
| | | Mean | Maximum | Minimum |
| | | (Micrograms $m^{-3}$) | | |
| Cadmium | 31 | 0.012 | 0.295 | 0.00 |
| Chromium | 31 | 0.005 | 0.024 | 0.00 |
| Cobalt | 31 | 0.0 | 0.0 | 0.0 |
| Copper | 31 | 0.12 | 0.60 | 0.02 |
| Iron | 31 | 1.50 | 3.20 | 0.80 |
| Lead | 31 | 2.34 | 4.06 | 0.87 |
| Manganese | 31 | 0.028 | 0.05 | 0.01 |
| Tin | 23 | 0.0 | 0.0 | 0.0 |
| Titanium | 31 | 0.078 | 0.13 | 0.03 |
| Vanadium | 31 | 0.010 | 0.033 | 0.00 |
| Sulfates | 28 | 10.66 | 21.20 | 3.87 |
| Nitrates | 28 | 8.42 | 13.75 | 3.24 |
| Ammonium Ion | 28 | 0.75 | 3.80 | 0.015 |
| TSP | 30 | 108.00 | 164.30 | 68.00 |

Note: All samples are 24 hour averages

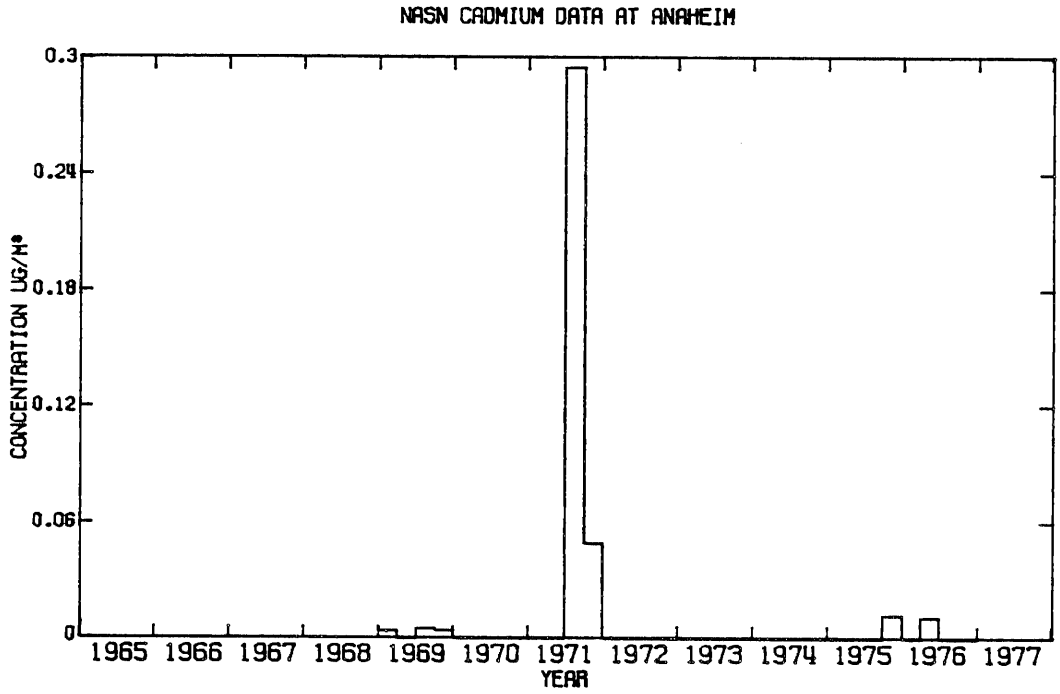



FIGURE A.10.1

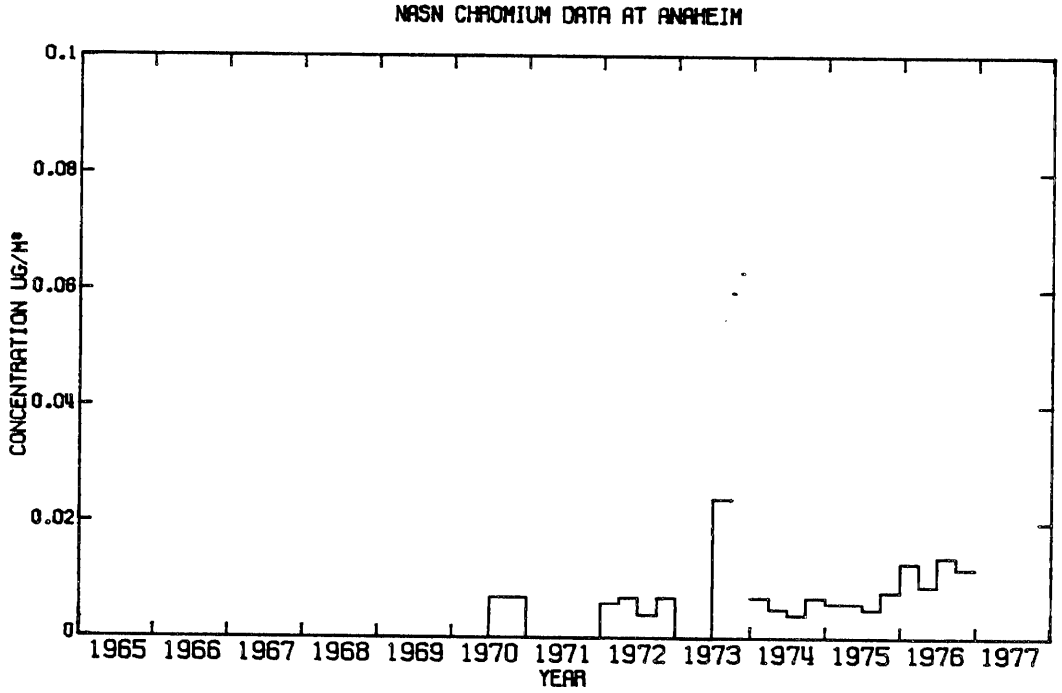



FIGURE A.10.2

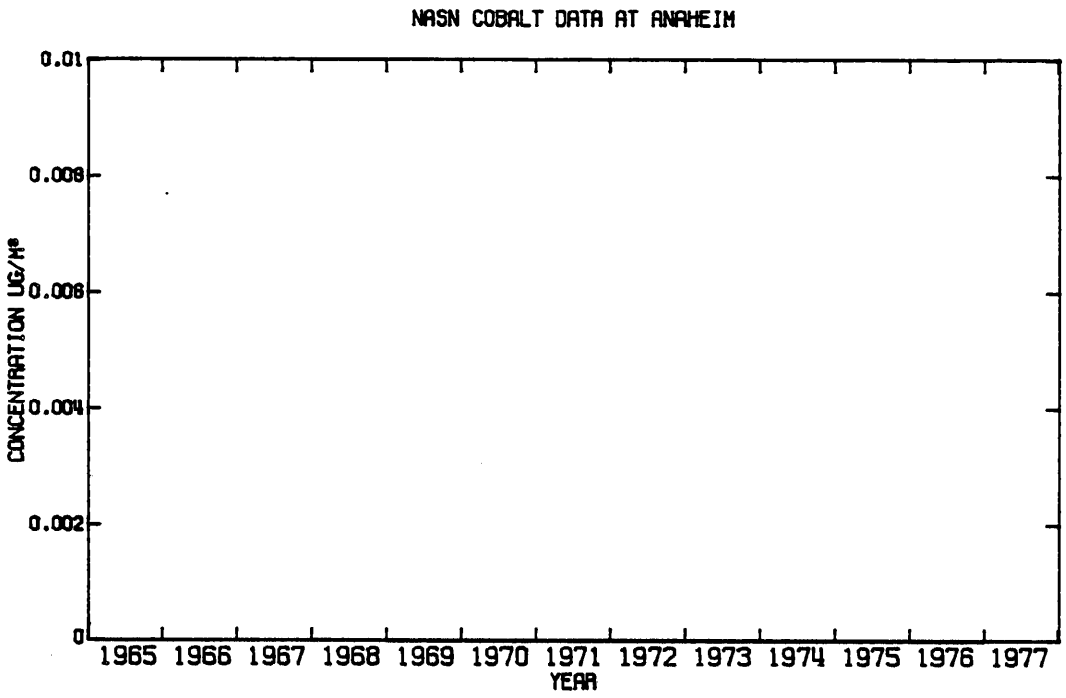



FIGURE A.10.3

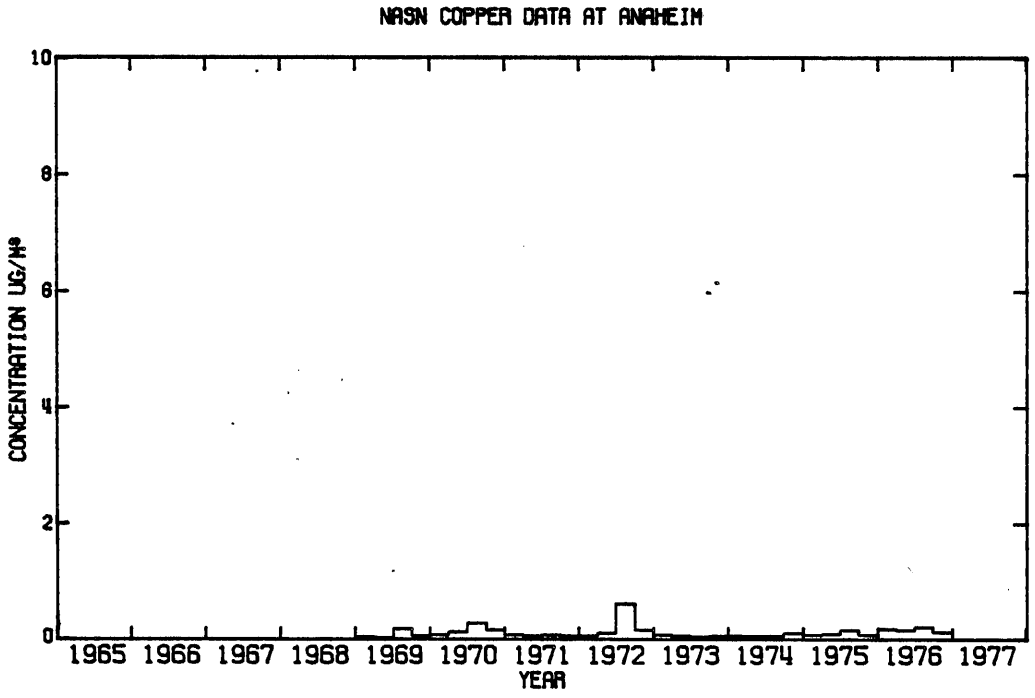



FIGURE A.10.4

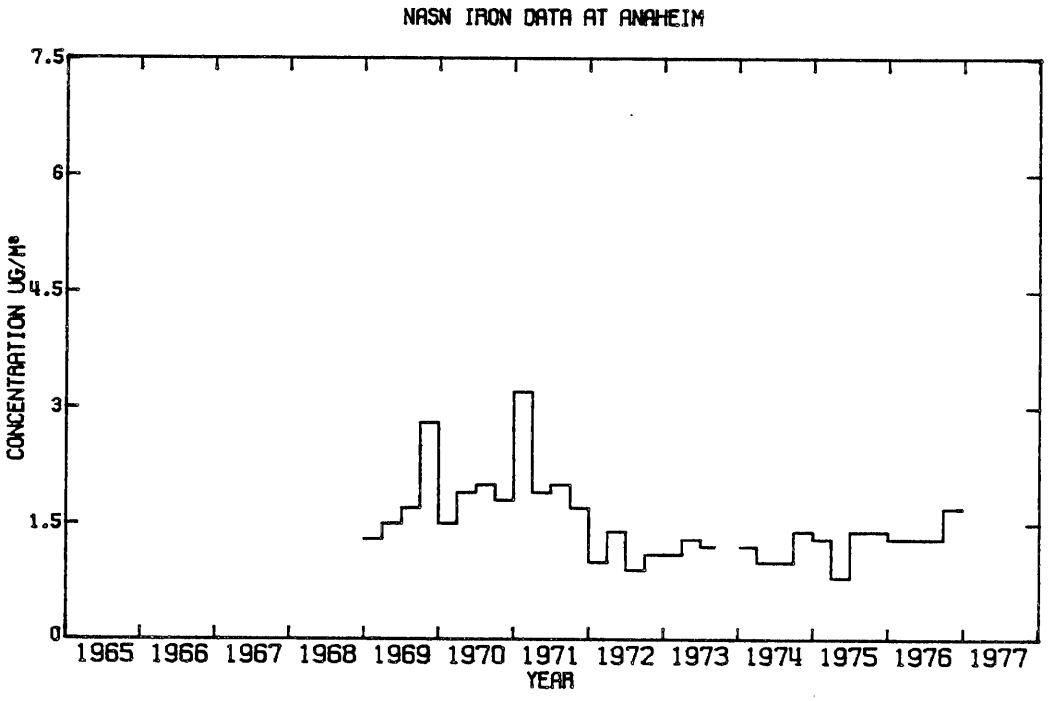



FIGURE A.10.5

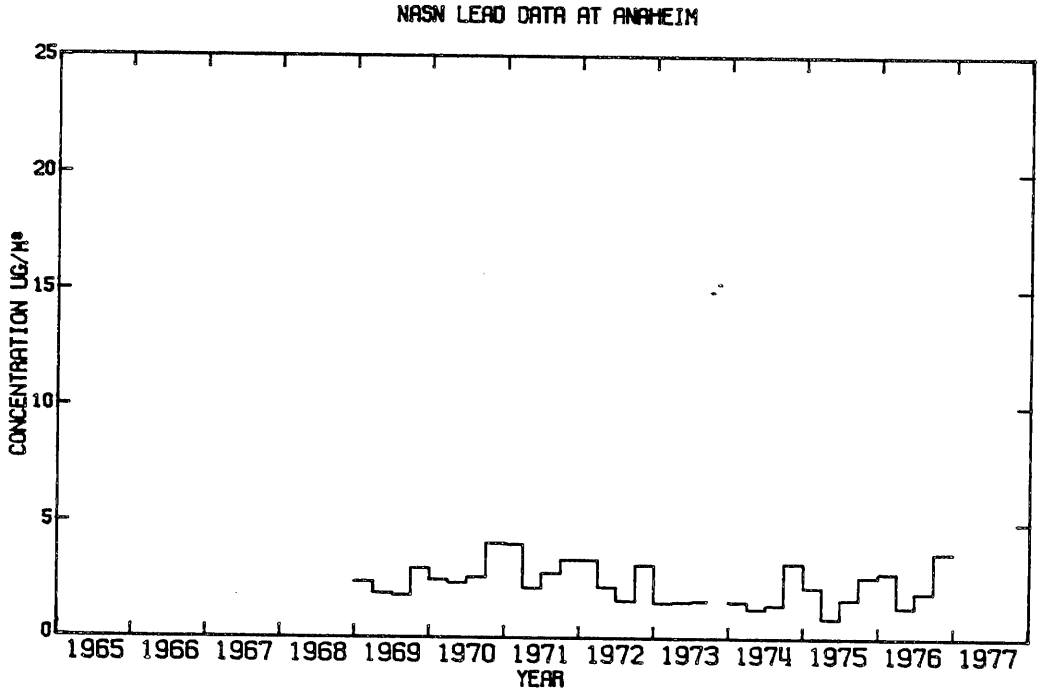



FIGURE A.10.6

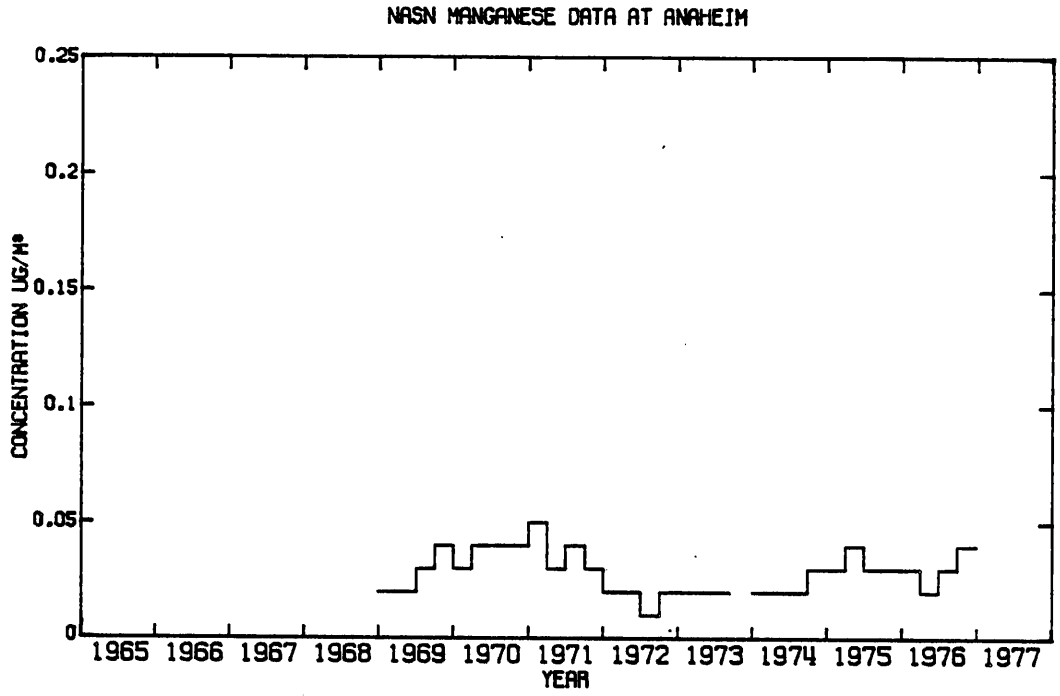



FIGURE A.10.7

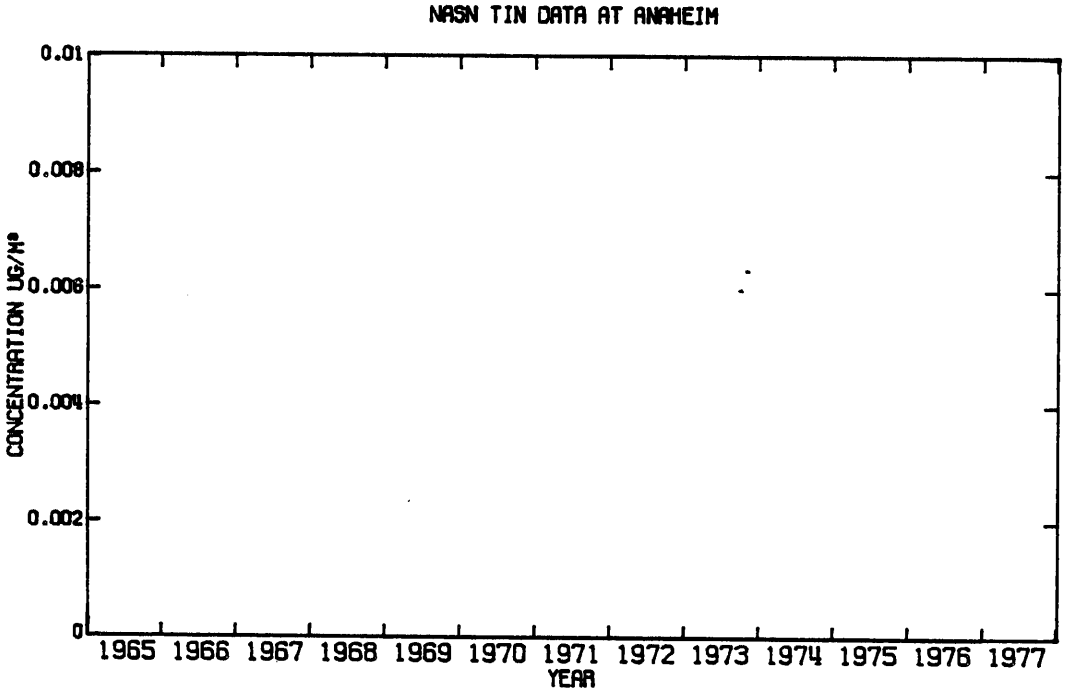



FIGURE A.10.8

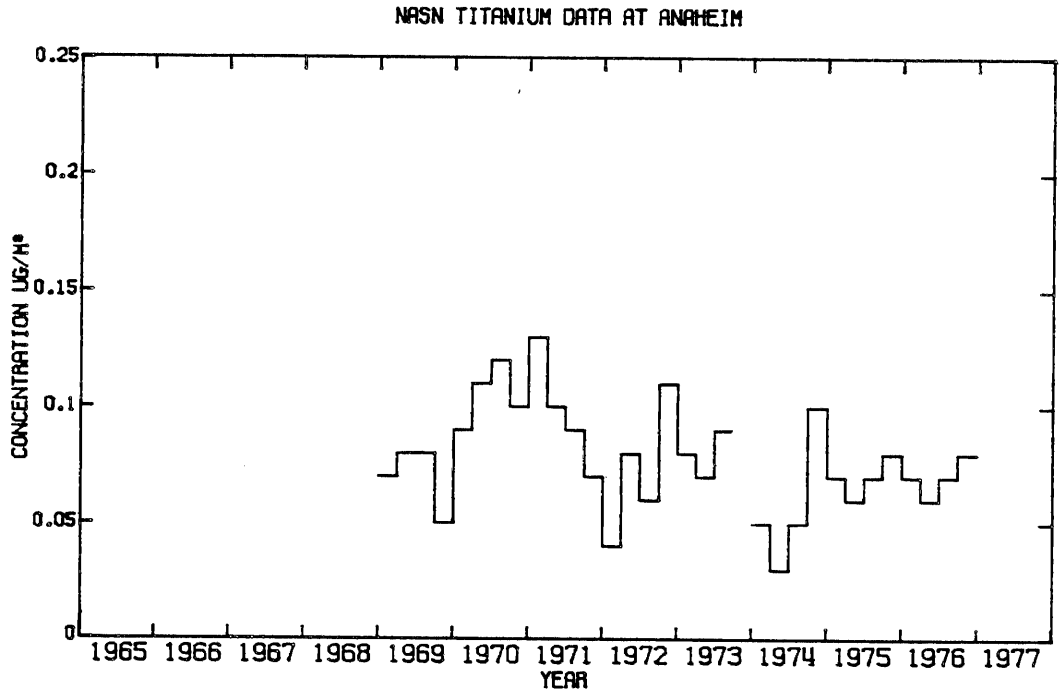



FIGURE A.10.9

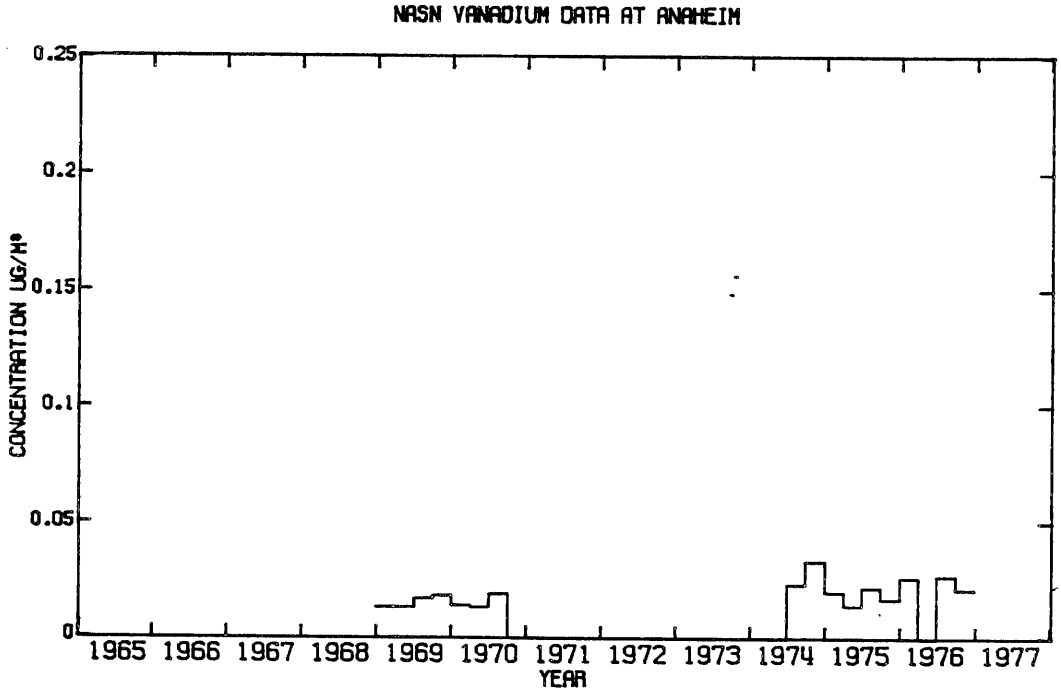



FIGURE A.10.10

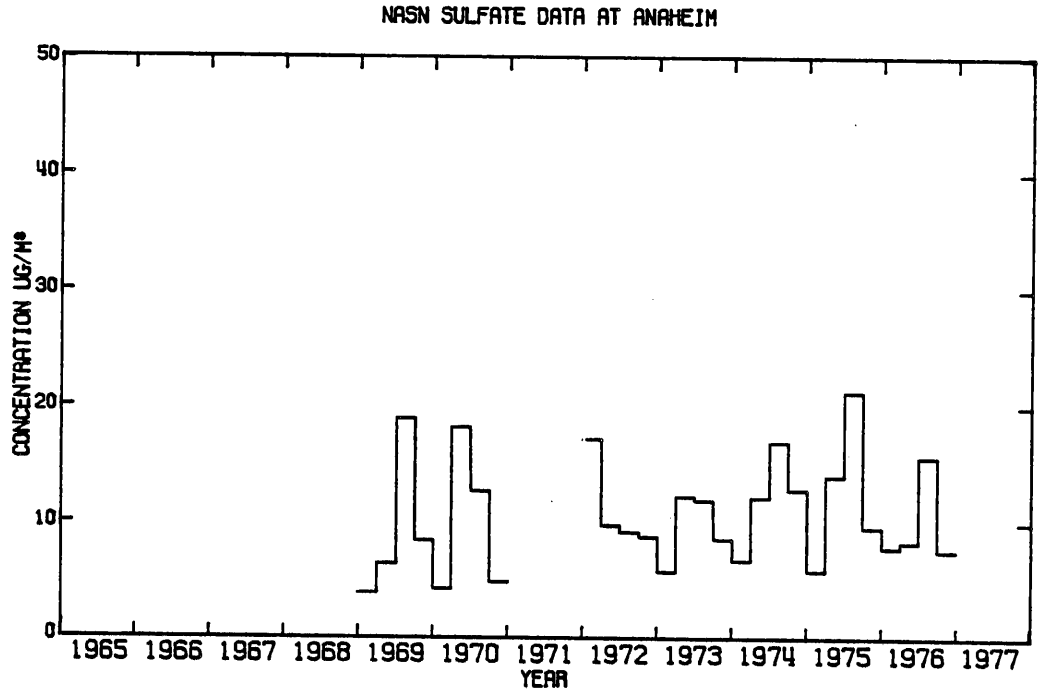



FIGURE A.10.11

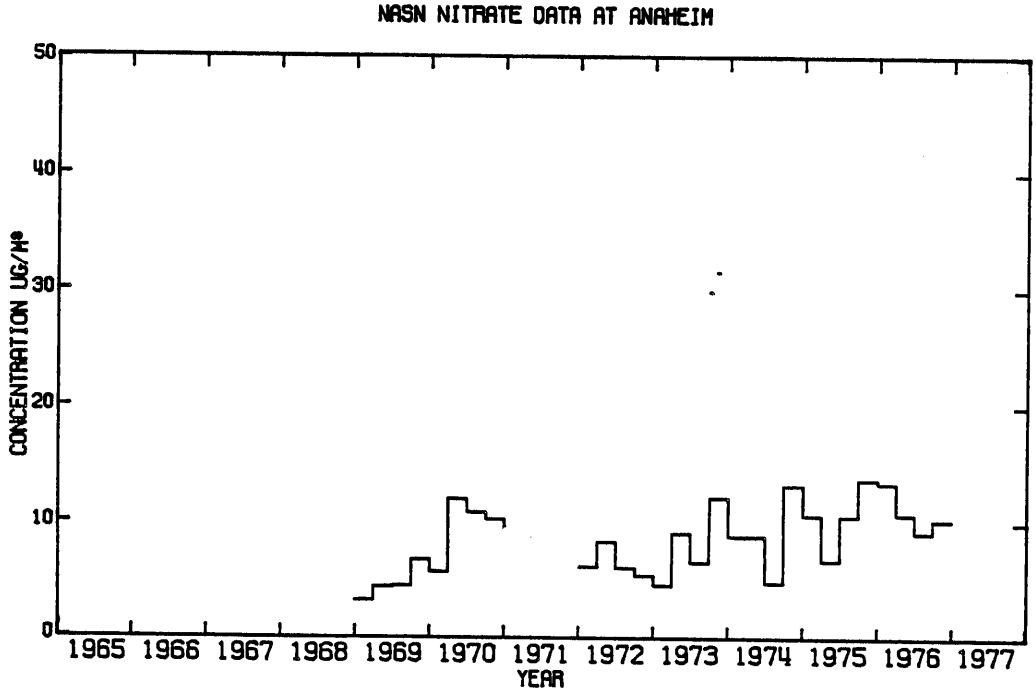



FIGURE A.10.12

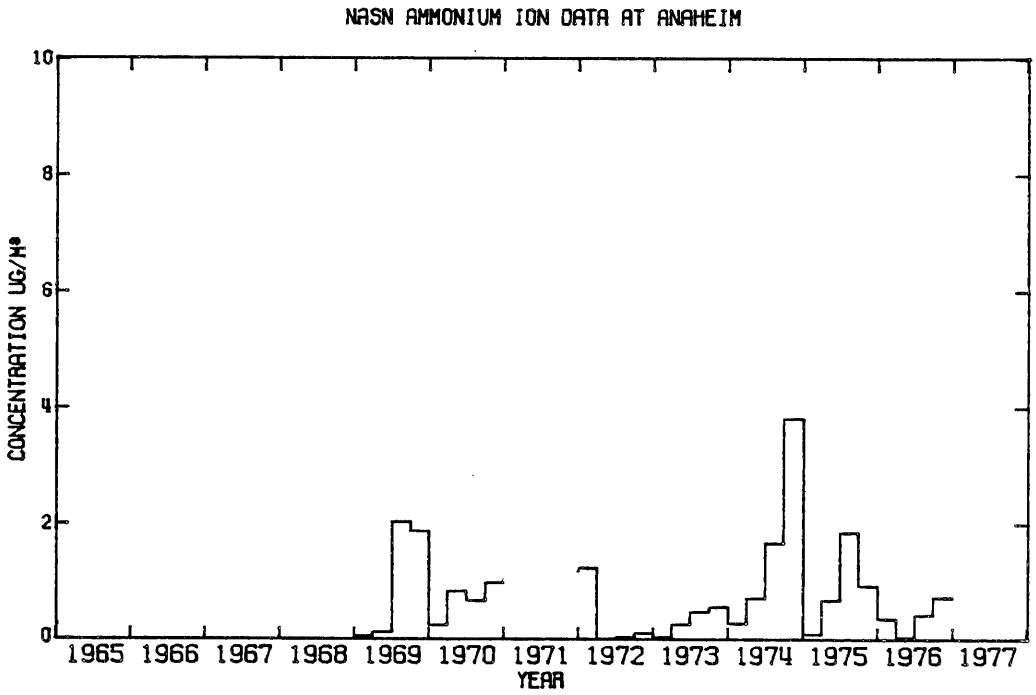



FIGURE A.10.13

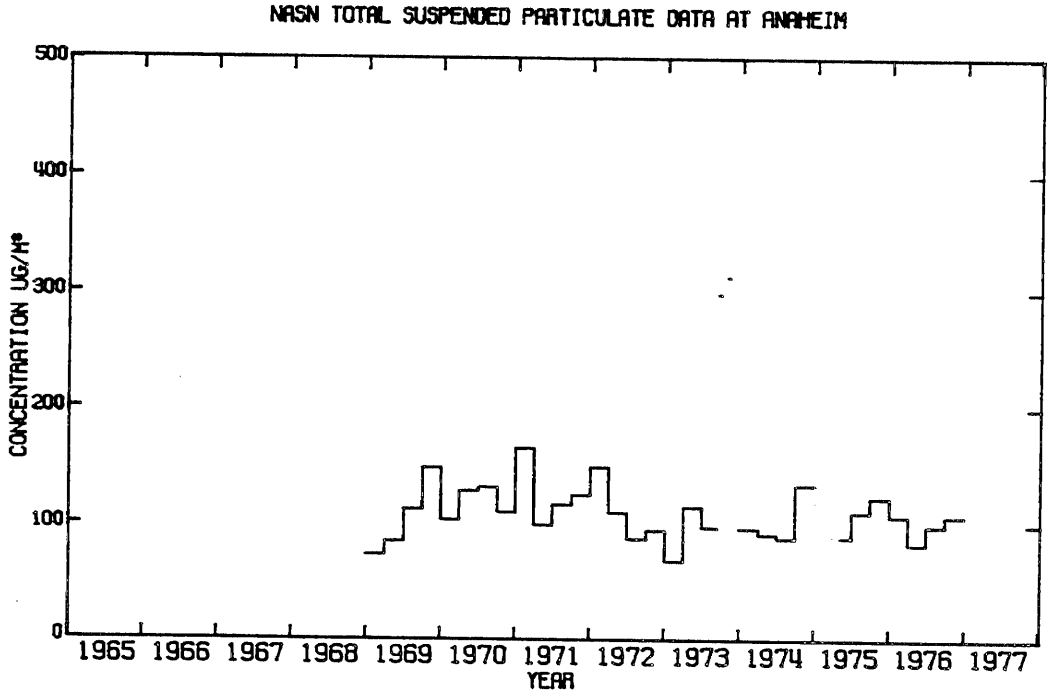



FIGURE A.10.14

## A.11 Monitoring Data at Downtown Los Angeles Site (NASN)

TABLE A.11.1

Particulate Data Available for Downtown Los Angeles Monitoring Site (NASN)

| Particulate Measurement | Figure |
|---|---|
| Cadmium | A.11.1 |
| Chromium | A.11.2 |
| Cobalt | A.11.3 |
| Copper | A.11.4 |
| Iron | A.11.5 |
| Lead | A.11.6 |
| Manganese | A.11.7 |
| Tin | A.11.8 |
| Titanium | A.11.9 |
| Vanadium | A.11.10 |
| Sulfates | A.11.11 |
| Nitrates | A.11.12 |
| Ammonium Ion | A.11.13 |
| Total Suspended Particulate | A.11.14 |

TABLE A.11.2

Summary of Particulate Air Quality Statistics
at Downtown Los Angeles Monitoring Site (NASN)
(1965 - 1976)

| Chemical Species | Number of Samples | Statistics | | |
|---|---|---|---|---|
| | | Mean | Maximum | Minimum |
| | | (Micrograms $m^{-3}$) | | |
| Cadmium | 38 | 0.002 | 0.002 | 0.00 |
| Chromium | 42 | 0.0115 | 0.03 | 0.00 |
| Cobalt | 42 | 0.0 | 0.0 | 0.0 |
| Copper | 42 | 0.096 | 0.25 | 0.03 |
| Iron | 42 | 1.71 | 3.40 | 0.70 |
| Lead | 42 | 3.60 | 11.00 | 1.24 |
| Manganese | 42 | 0.033 | 0.06 | 0.02 |
| Tin | 35 | 0.0014 | 0.021 | 0.00 |
| Titanium | 42 | 0.056 | 0.130 | 0.00 |
| Vanadium | 42 | 0.011 | 0.062 | 0.00 |
| Sulfates | 48 | 11.63 | 20.54 | 3.83 |
| Nitrates | 44 | 10.52 | 21.95 | 2.97 |
| Ammonium Ion | 44 | 1.07 | 4.98 | 0.04 |
| TSP | 47 | 124.64 | 214.00 | 36.00 |

Note: All samples are 24 hour averages

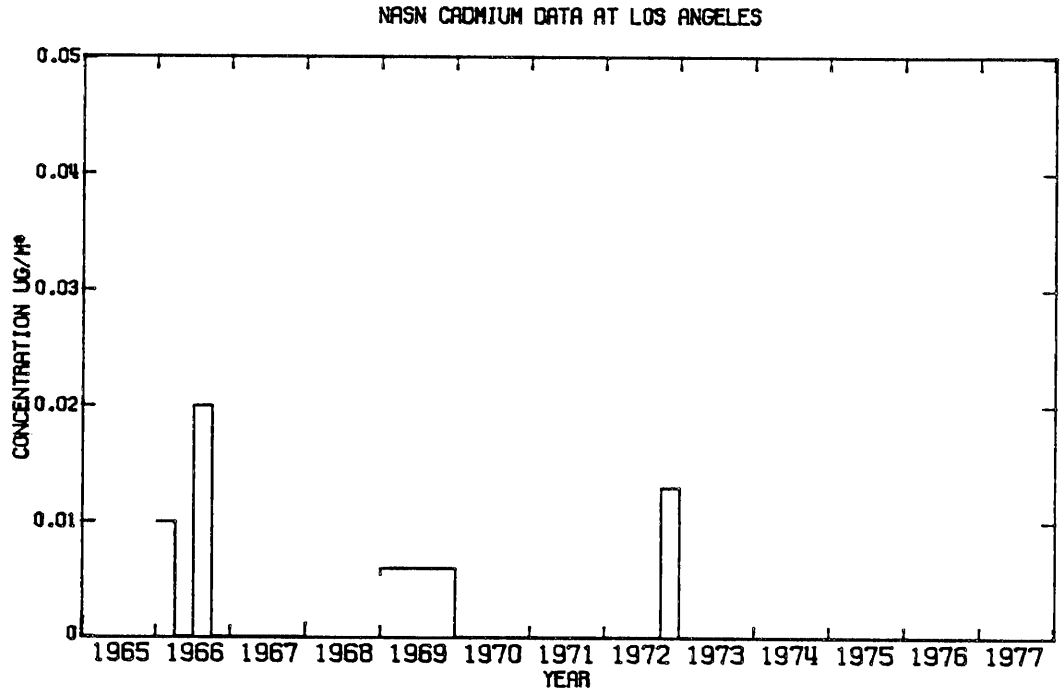



FIGURE A.11.1

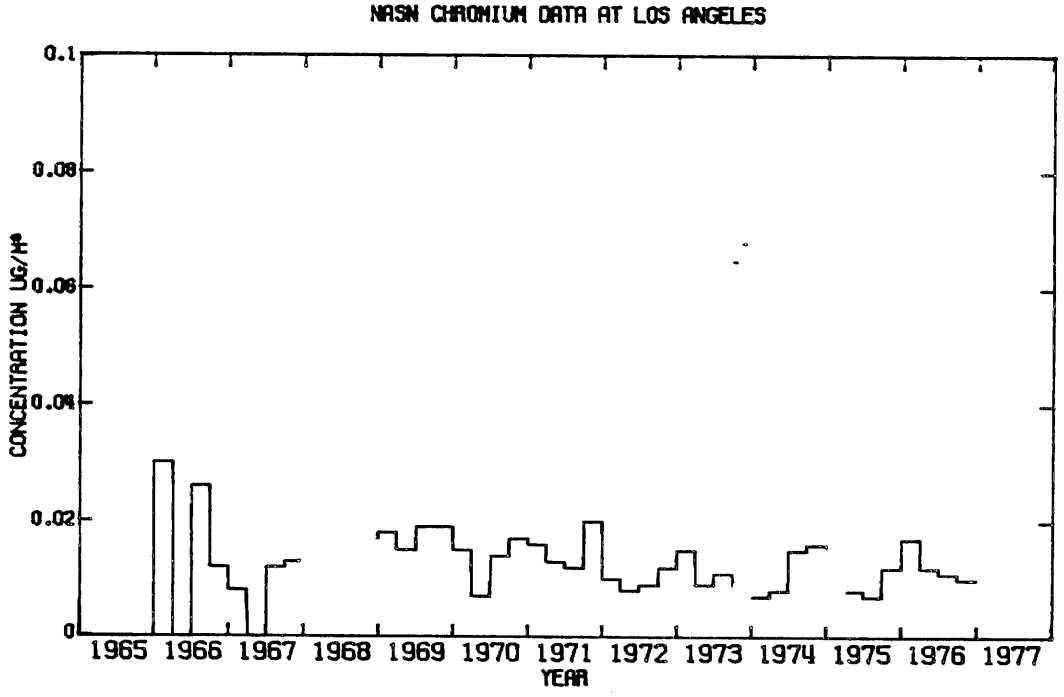



FIGURE A.11.2

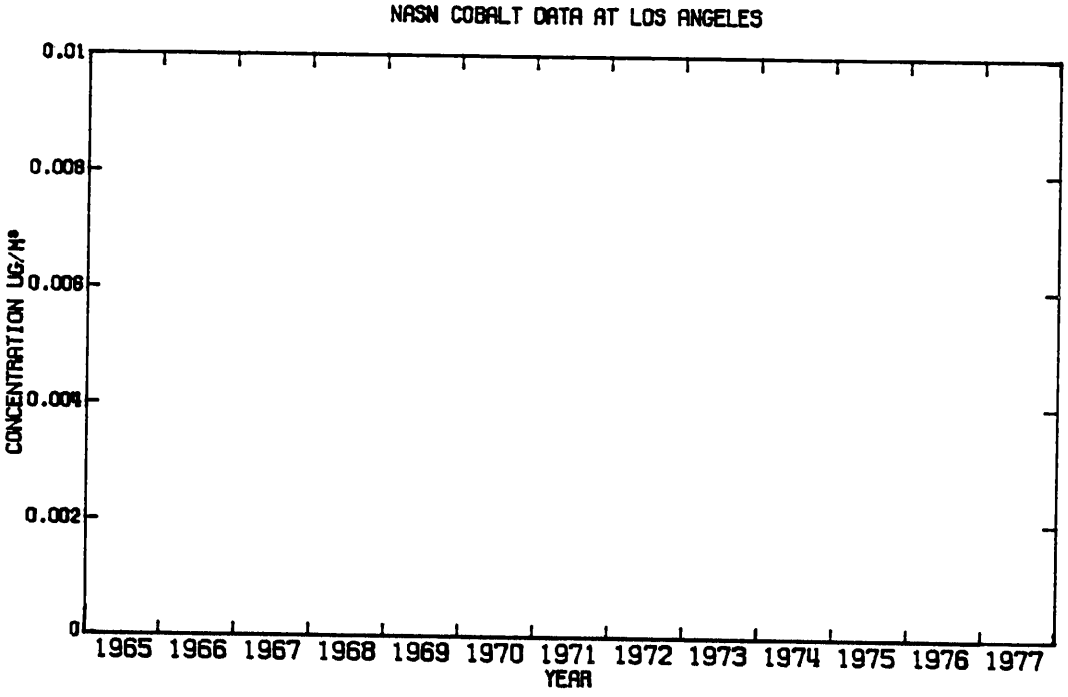



FIGURE A.11.3

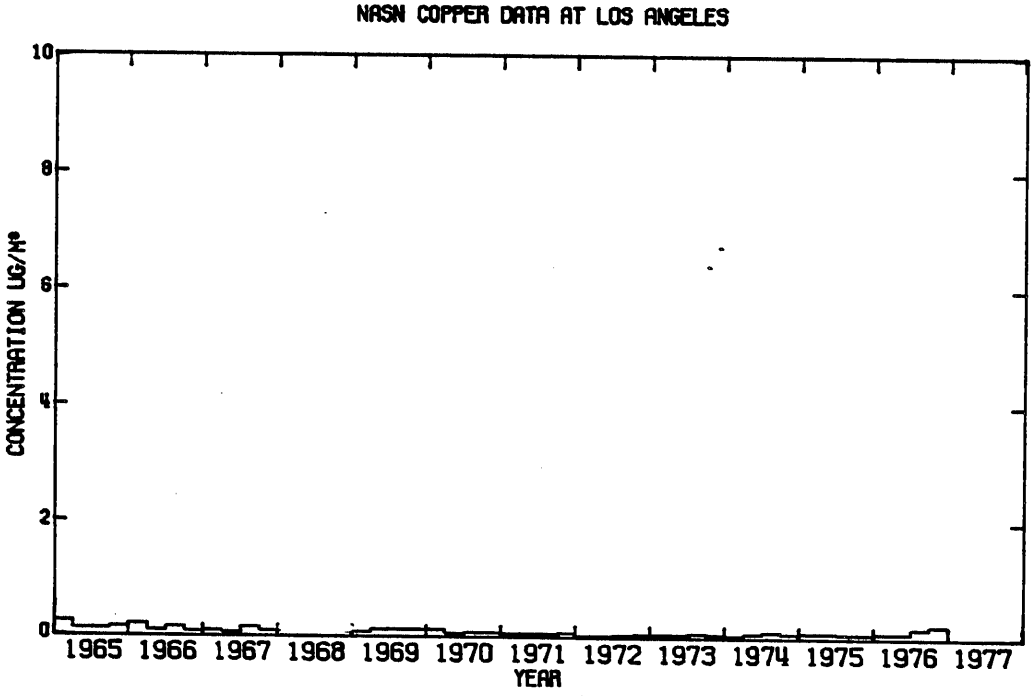



FIGURE A.11.4

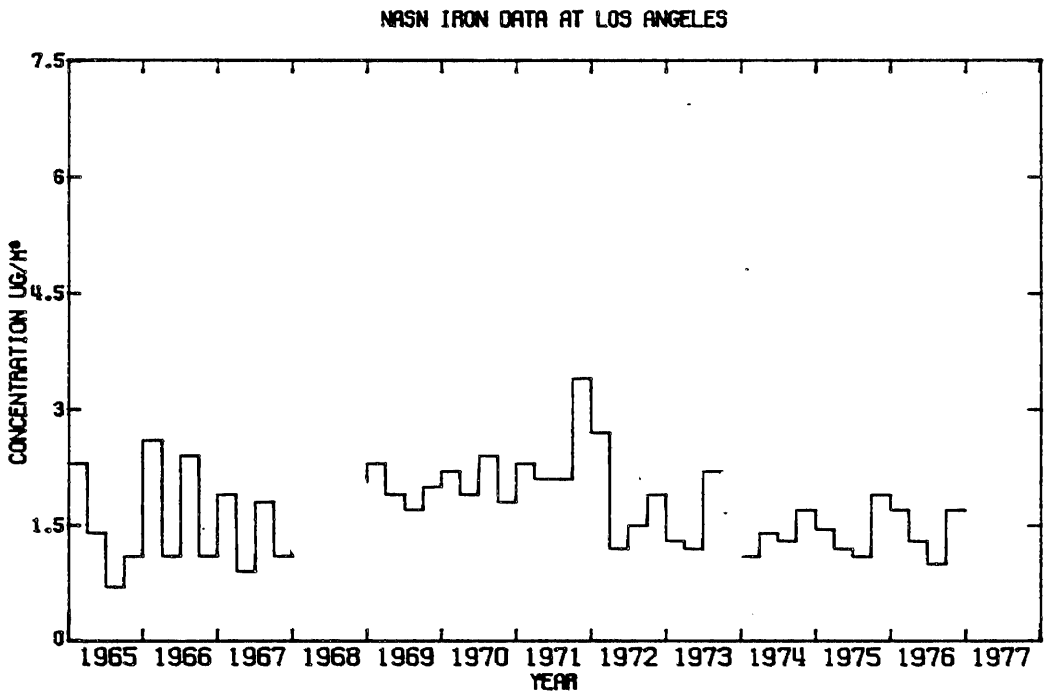



FIGURE A.11.5

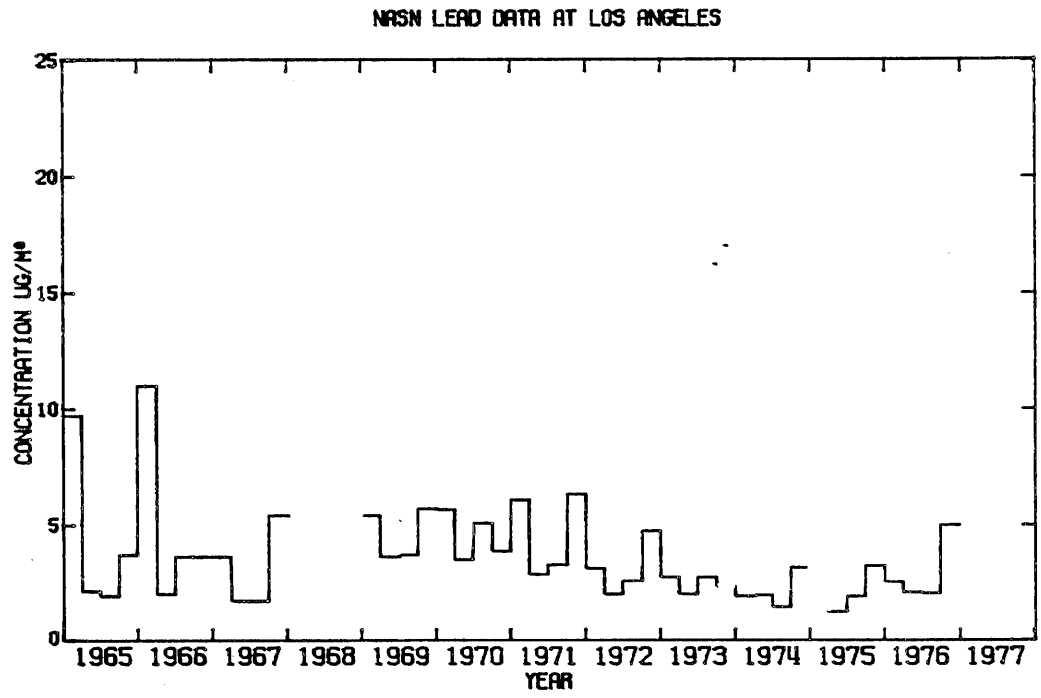



FIGURE A.11.6

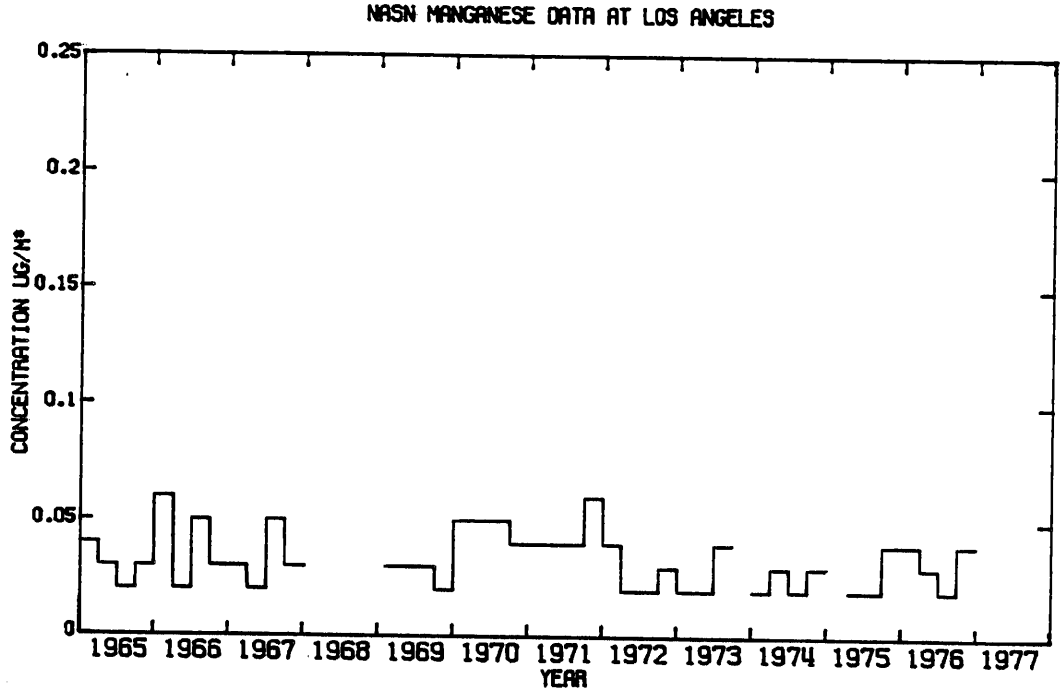



FIGURE A.11.7

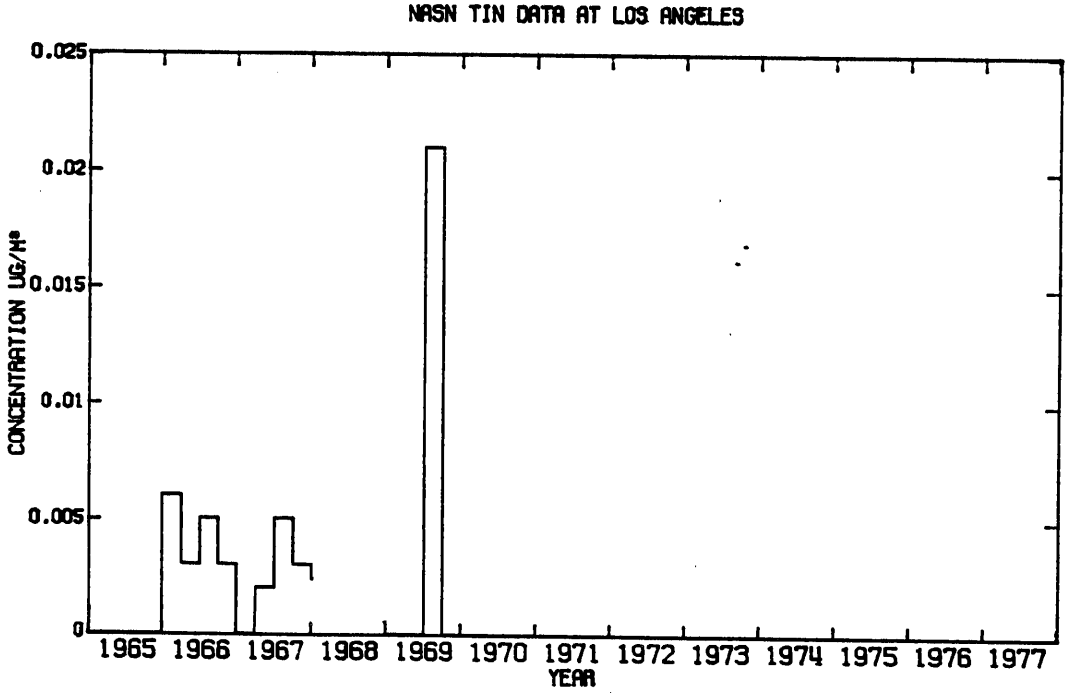



FIGURE A.11.8

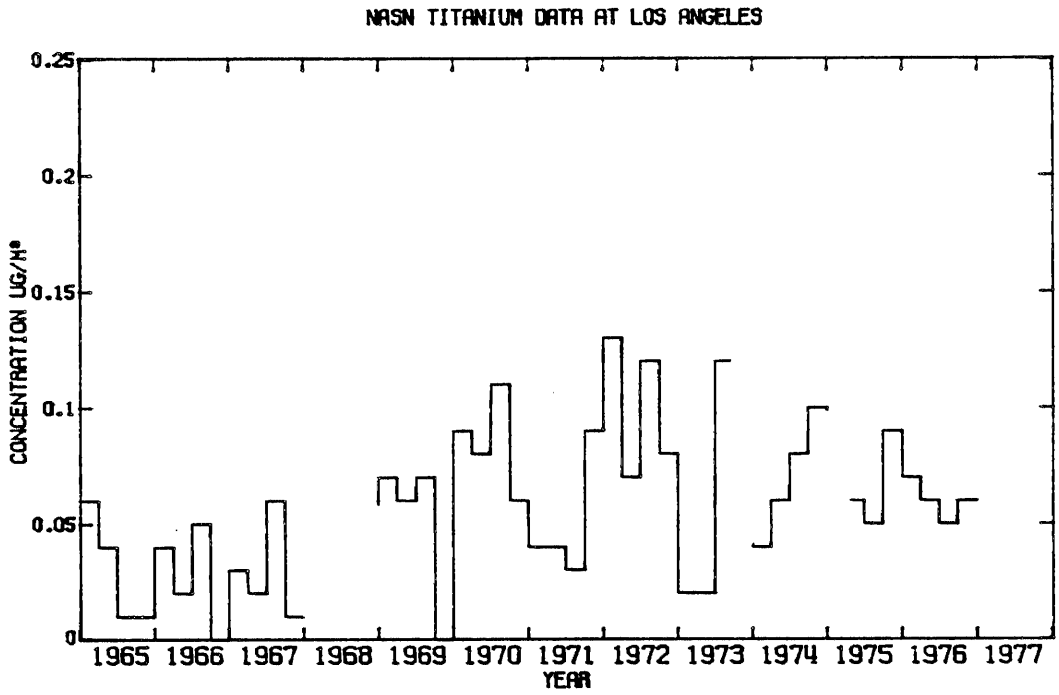



FIGURE A.11.9

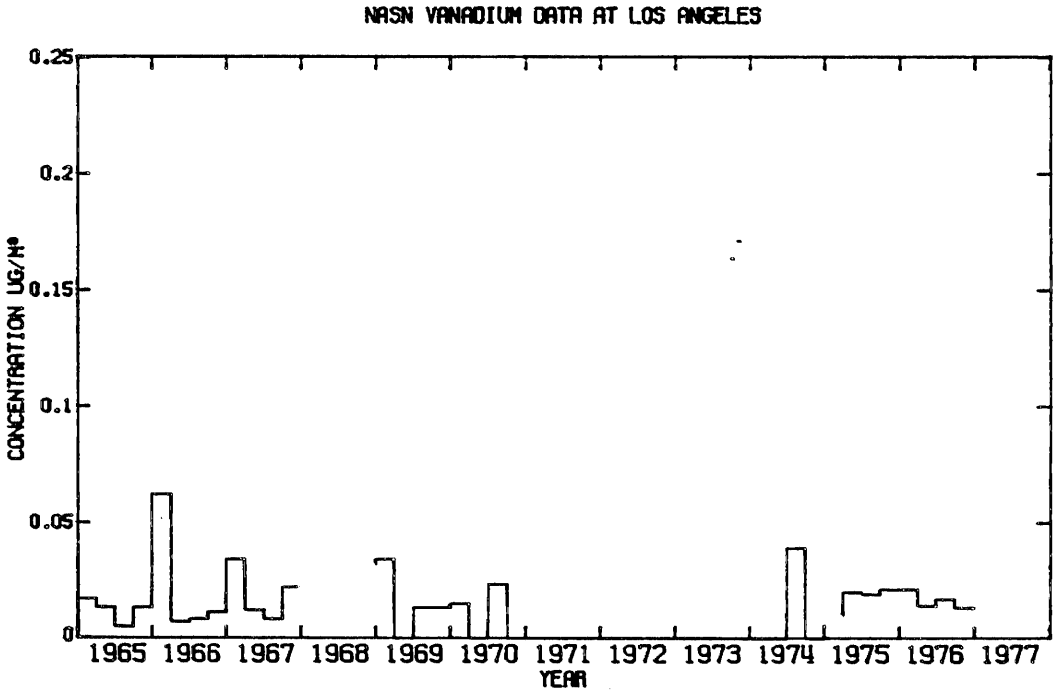



FIGURE A.11.10

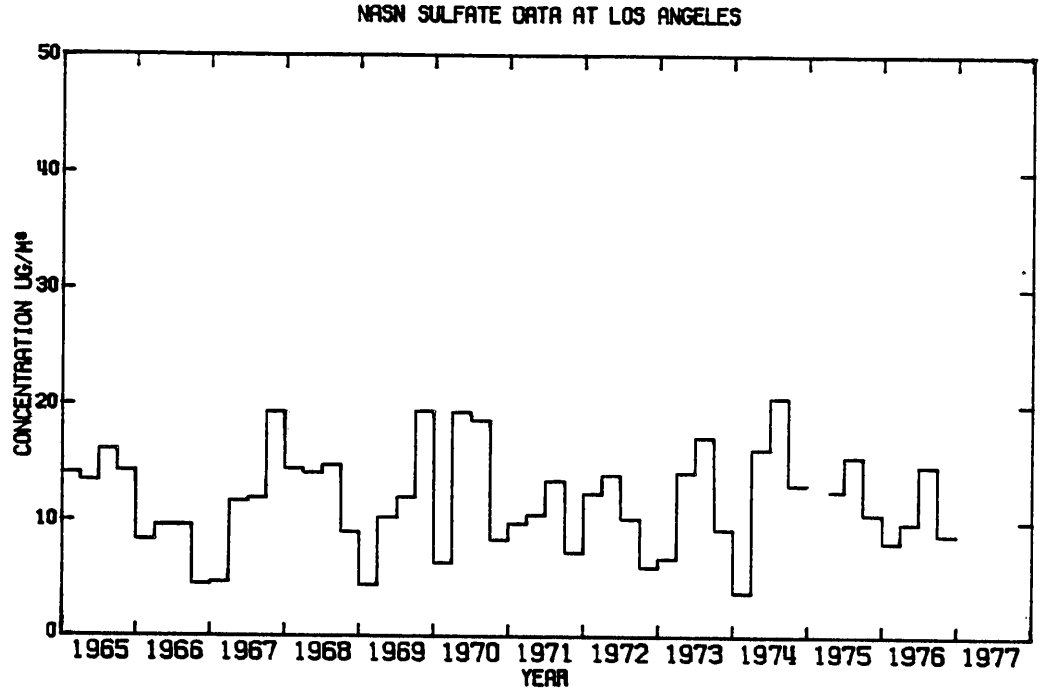



FIGURE A.11.11

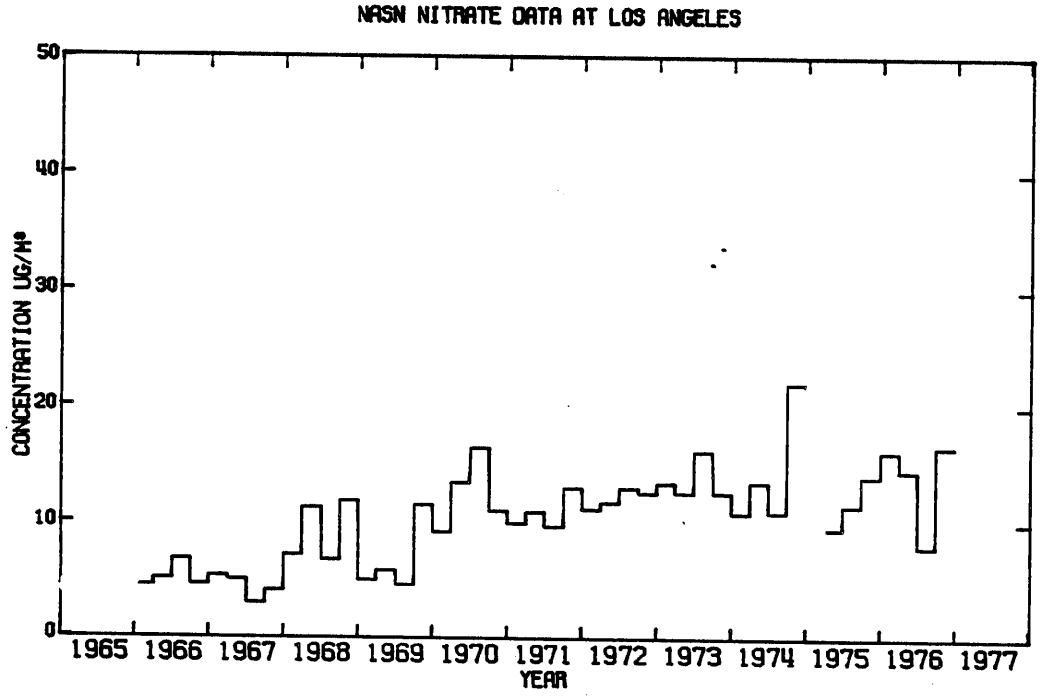



FIGURE A.11.12

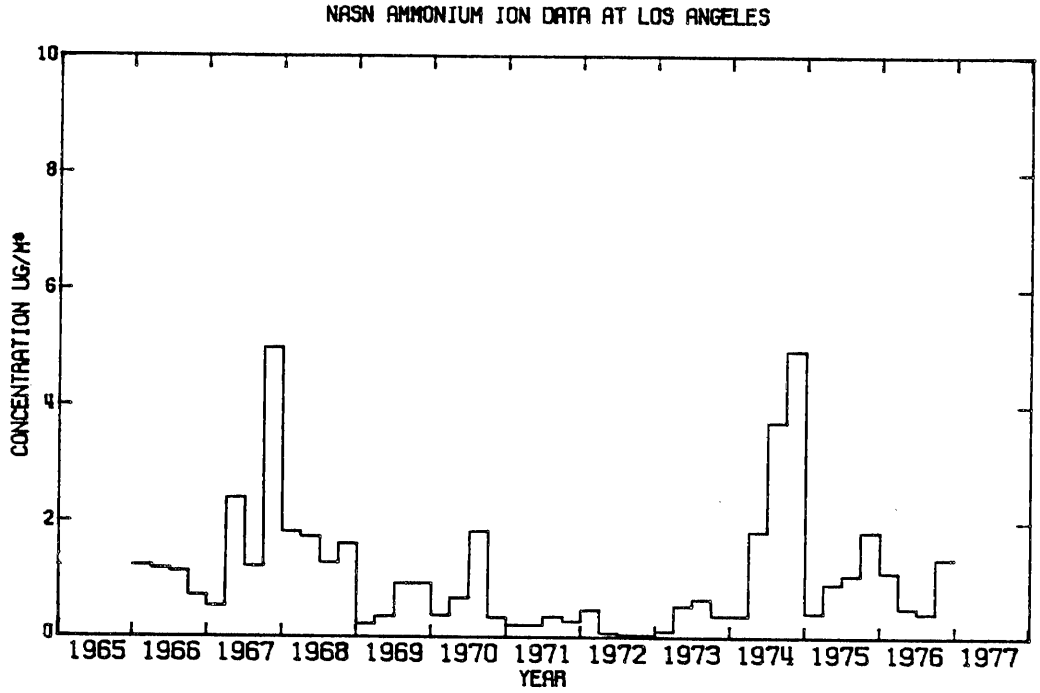



FIGURE A.11.13

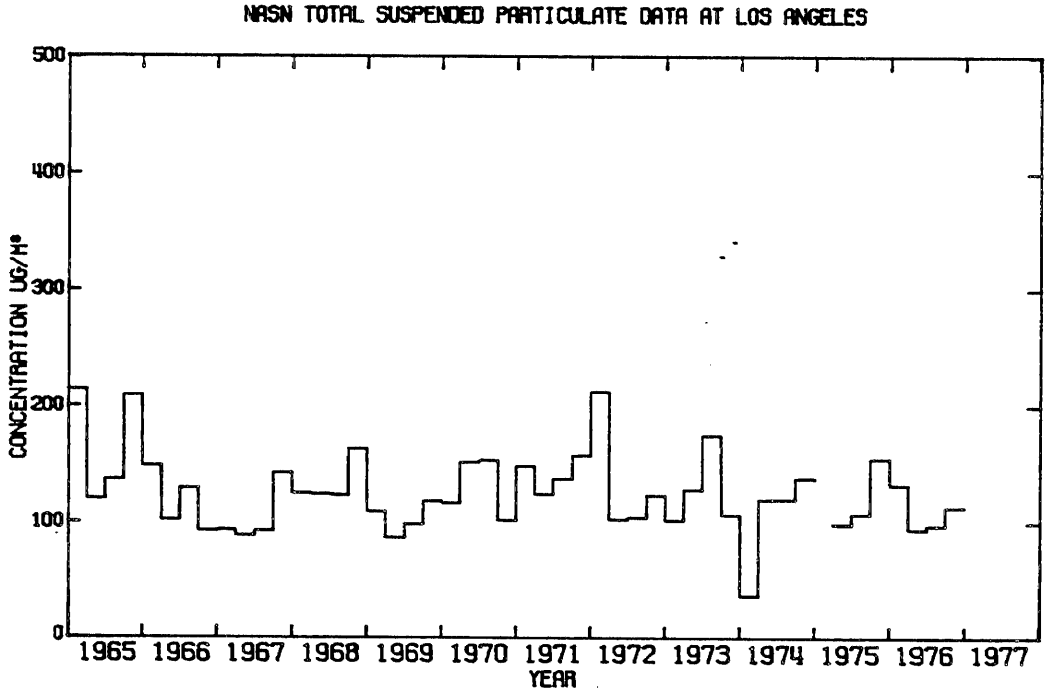



FIGURE A.11.14

## A.12 Monitoring Data at San Bernardino Site (NASN)

TABLE A.12.1

Particulate Data Available for San Bernardino Monitoring Site (NASN)

| Particulate Measurement | Figure |
|---|---|
| Cadmium | A.12.1 |
| Chromium | A.12.2 |
| Cobalt | A.12.3 |
| Copper | A.12.4 |
| Iron | A.12.5 |
| Lead | A.12.6 |
| Manganese | A.12.7 |
| Tin | A.12.8 |
| Titanium | A.12.9 |
| Vanadium | A.12.10 |
| Sulfates | A.12.11 |
| Nitrates | A.12.12 |
| Ammonium Ion | A.12.13 |
| Total Suspended Particulate | A.12.14 |

TABLE A.12.2

Summary of Particulate Air Quality Statistics
at San Bernardino Monitoring Site (NASN)
(1969 - 1976)

| Chemical Species | Number of Samples | Statistics | | |
|---|---|---|---|---|
| | | Mean | Maximum | Minimum |
| | | (Micrograms $m^{-3}$) | | |
| Cadmium | 31 | 0.0023 | 0.020 | 0.00 |
| Chromium | 31 | 0.014 | 0.028 | 0.00 |
| Cobalt | 31 | 0.0009 | 0.007 | 0.00 |
| Copper | 31 | 0.20 | 0.64 | 0.04 |
| Iron | 31 | 2.40 | 5.60 | 1.00 |
| Lead | 31 | 1.51 | 3.25 | 0.58 |
| Manganese | 31 | 0.051 | 0.11 | 0.02 |
| Tin | 23 | 0.0029 | 0.021 | 0.00 |
| Titanium | 31 | 0.098 | 0.26 | 0.00 |
| Vanadium | 31 | 0.0078 | 0.033 | 0.00 |
| Sulfates | 28 | 12.22 | 25.20 | 5.29 |
| Nitrates | 28 | 14.56 | 23.32 | 6.41 |
| Ammonium Ion | 28 | 1.26 | 3.70 | 0.02 |
| TSP | 31 | 130.44 | 238.20 | 64.40 |

Note: All samples are 24 hour averages

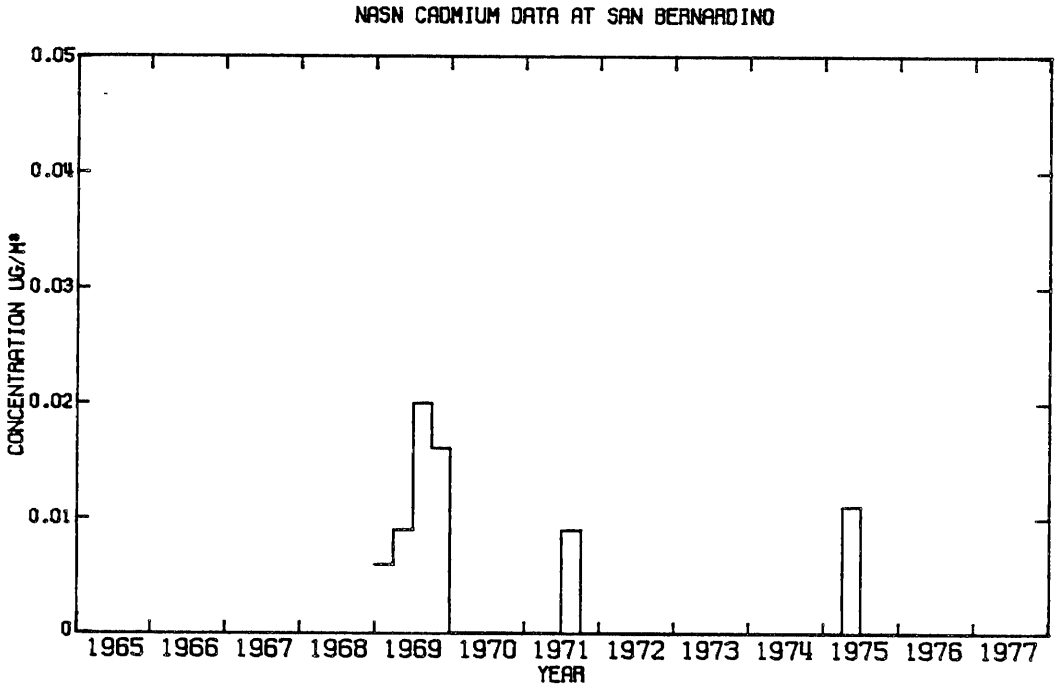



FIGURE A.12.1

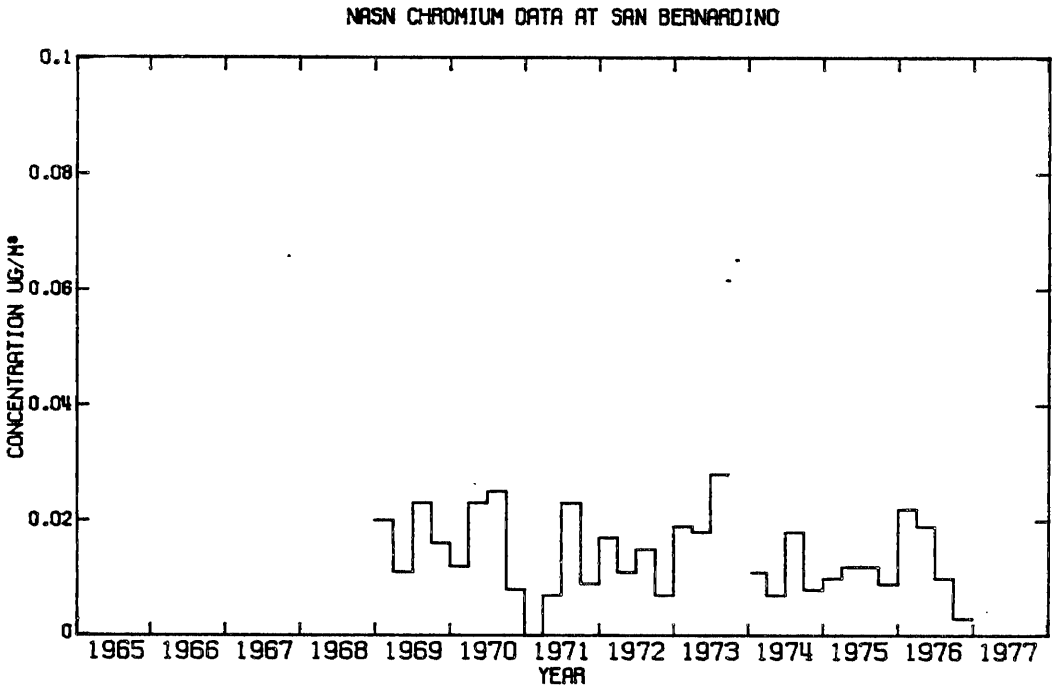



FIGURE A.12.2

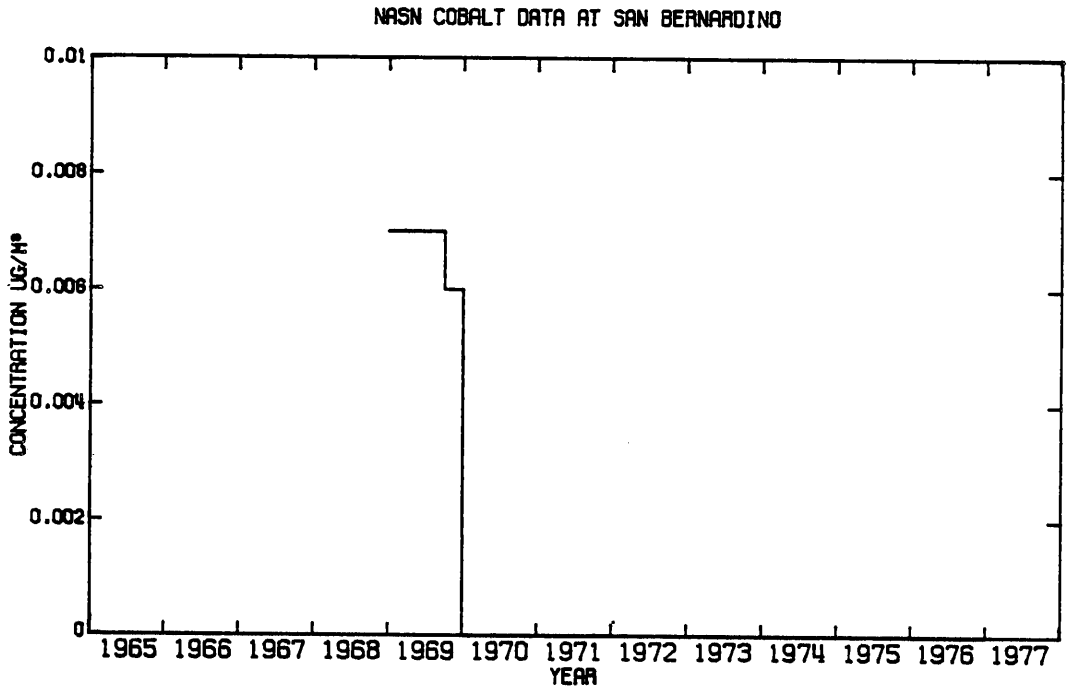



FIGURE A.12.3

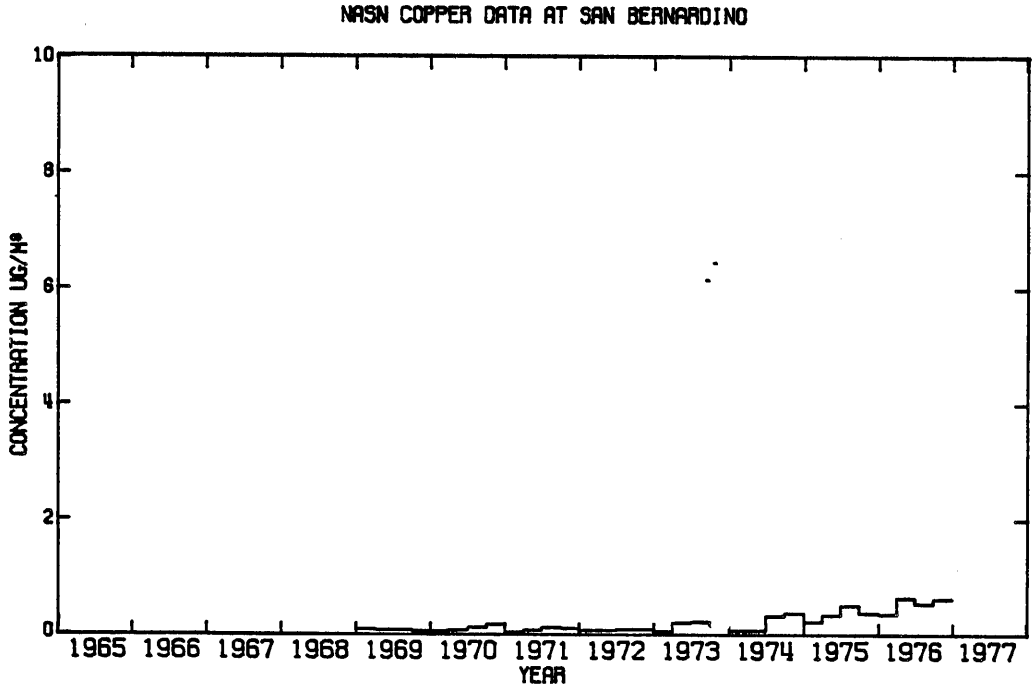



FIGURE A.12.4

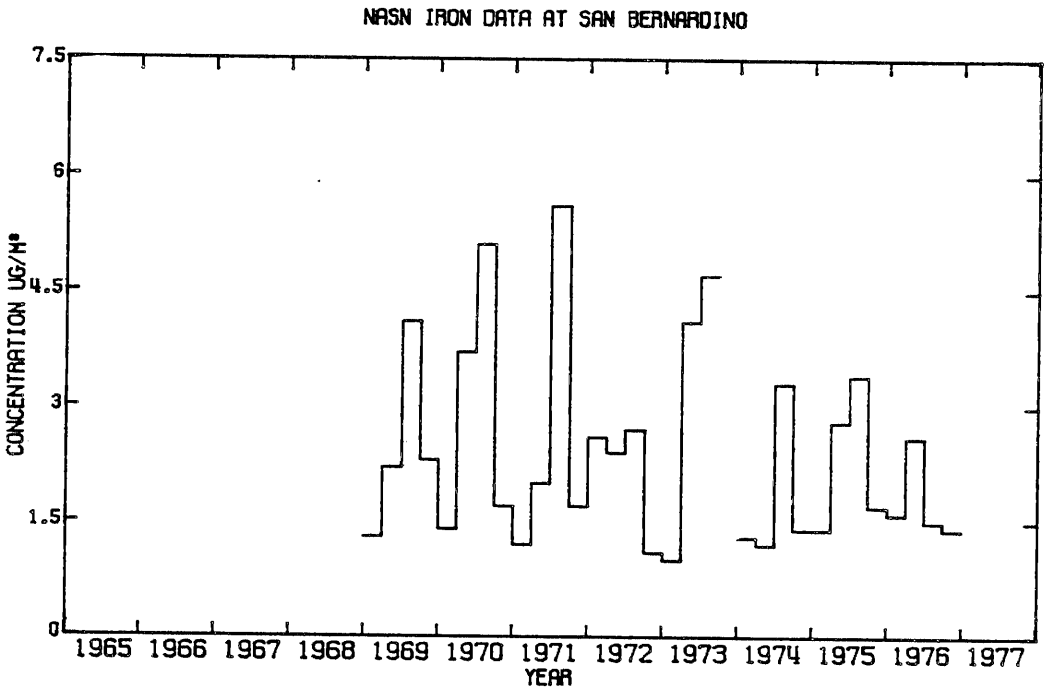



FIGURE A.12.5

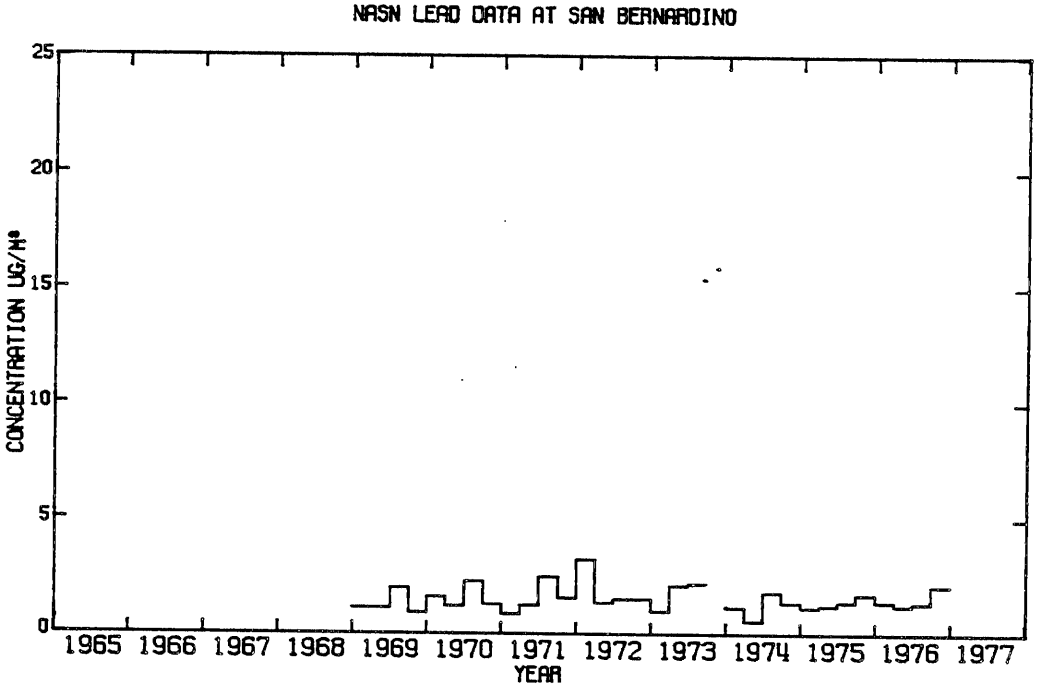



FIGURE A.12.6

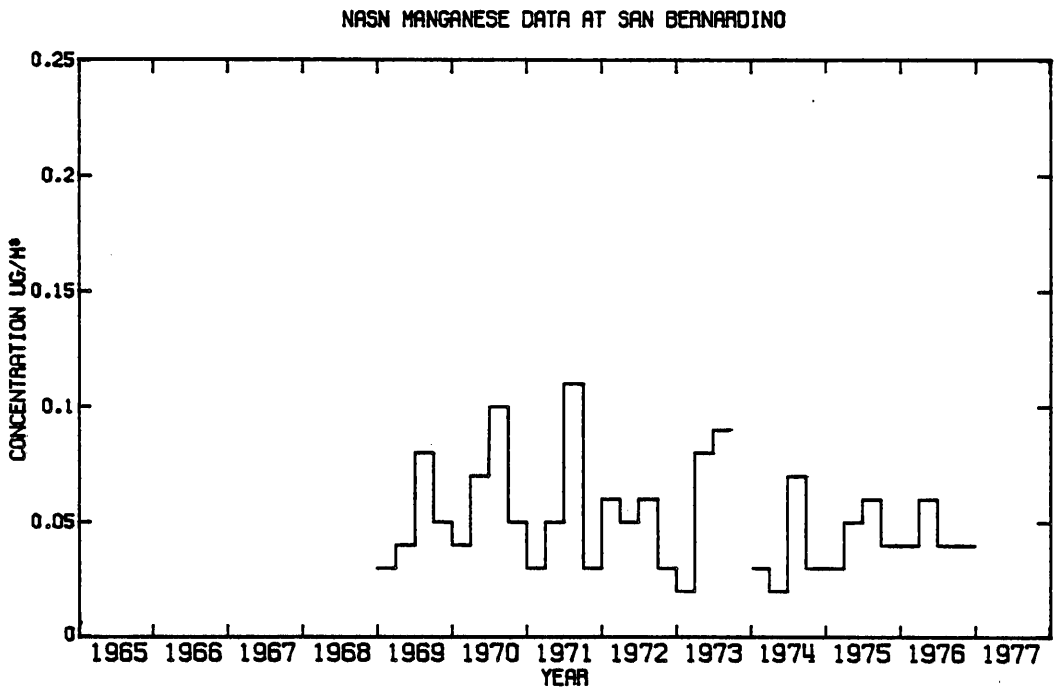



FIGURE A.12.7

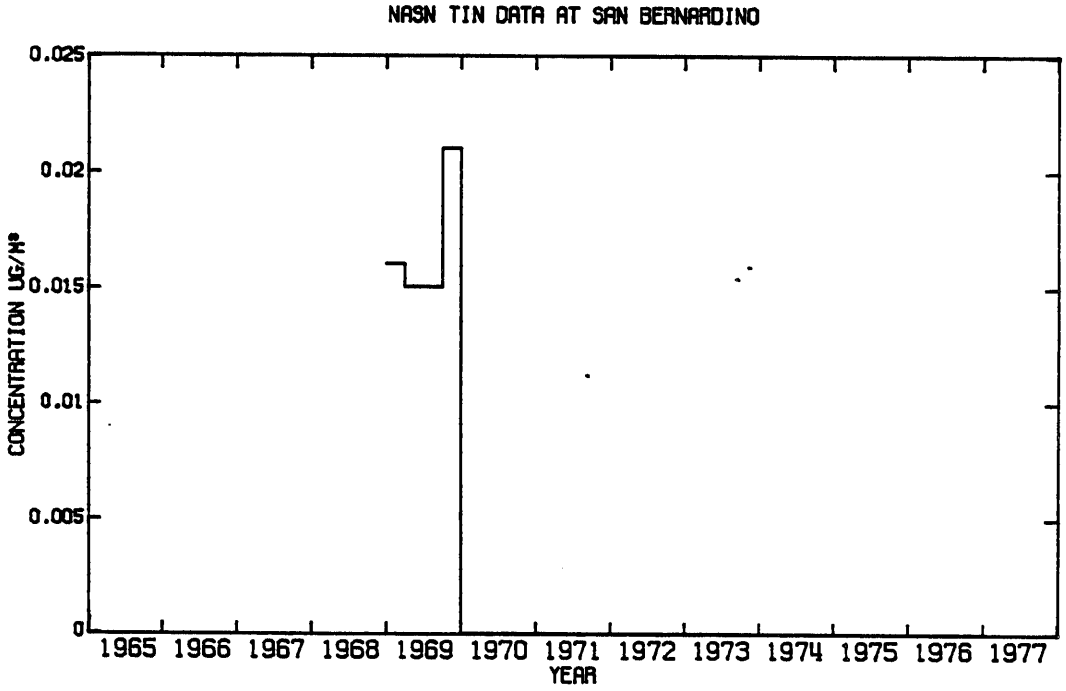



FIGURE A.12.8

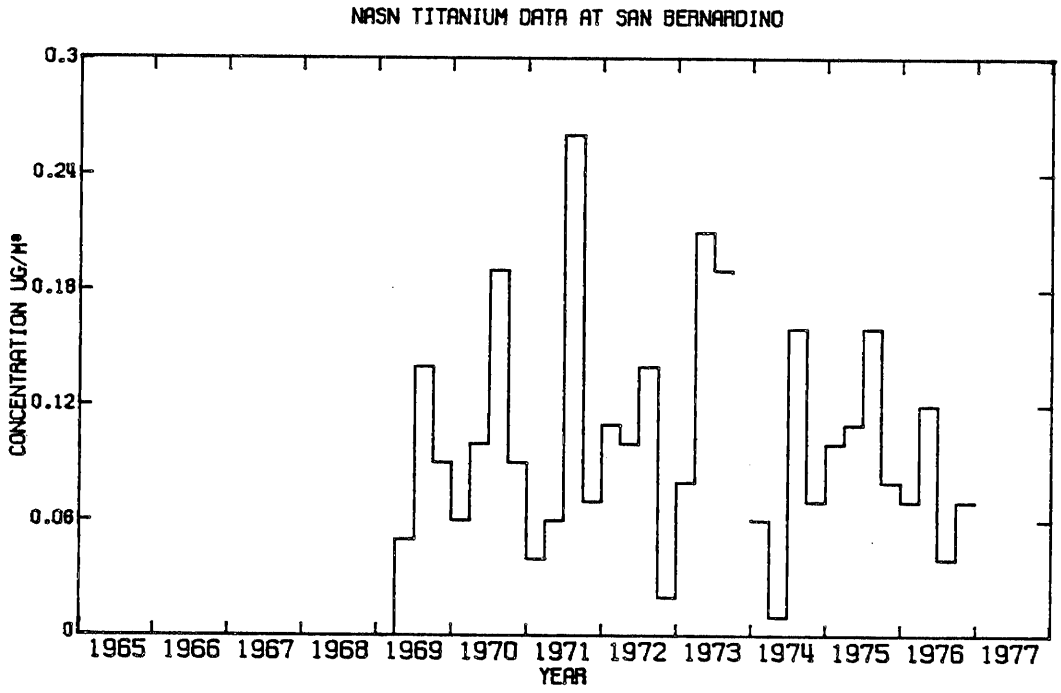



FIGURE A.12.9

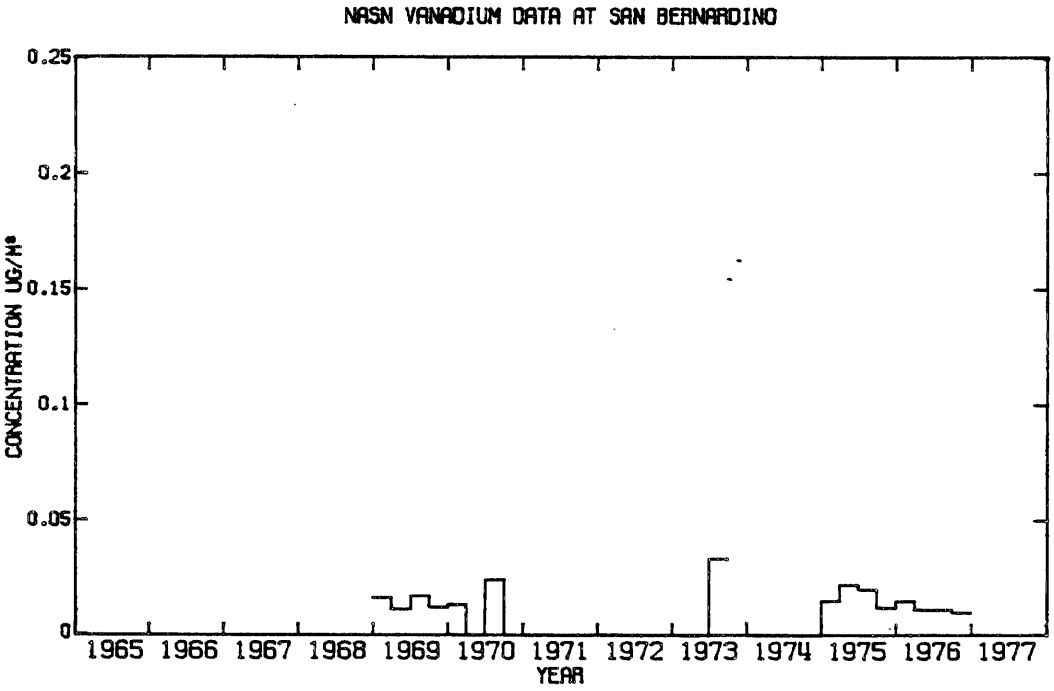



FIGURE A.12.10

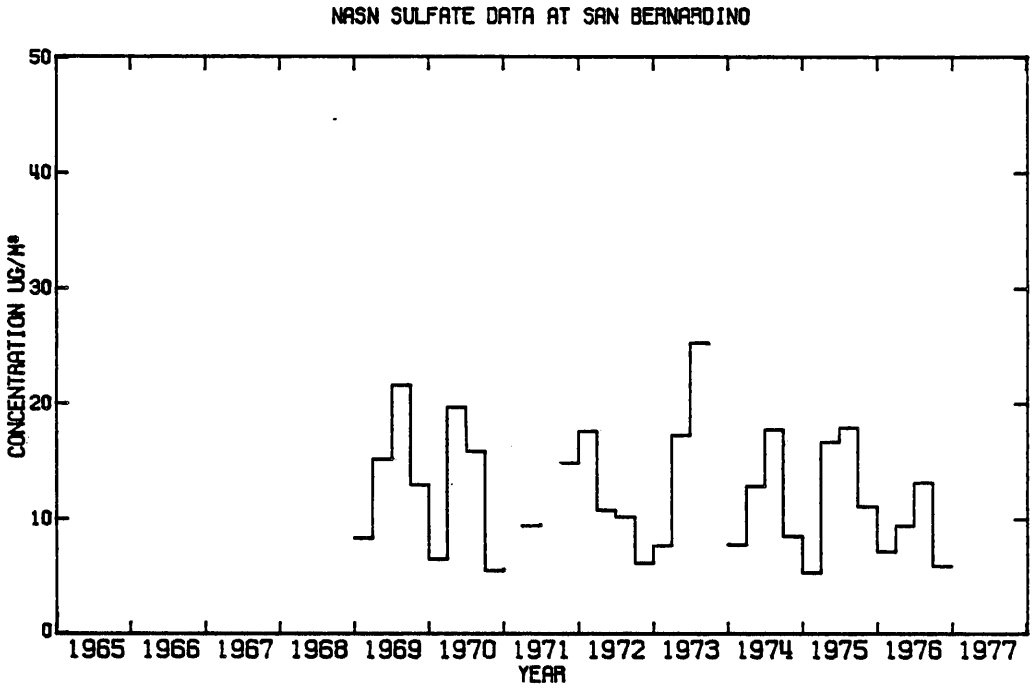



FIGURE A.12.11

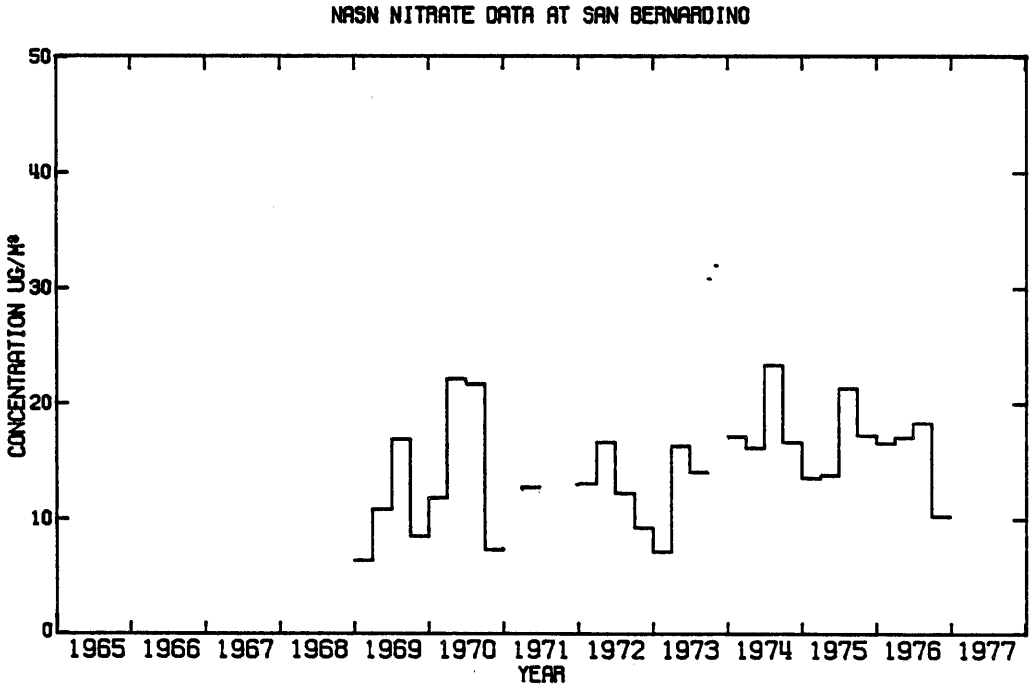



FIGURE A.12.12

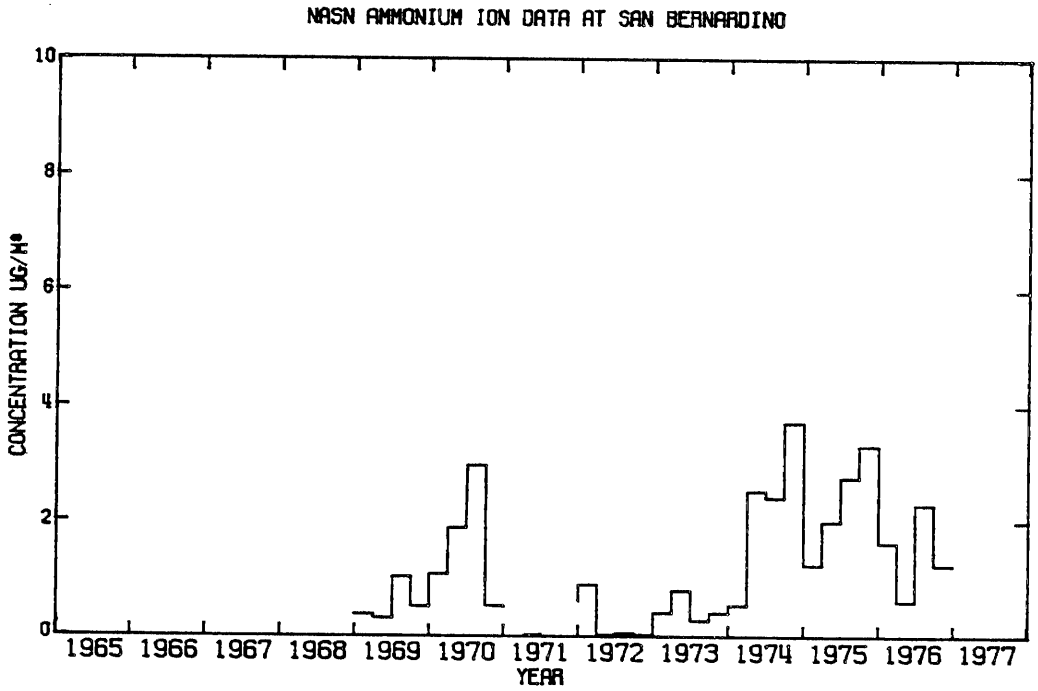



FIGURE A.12.13

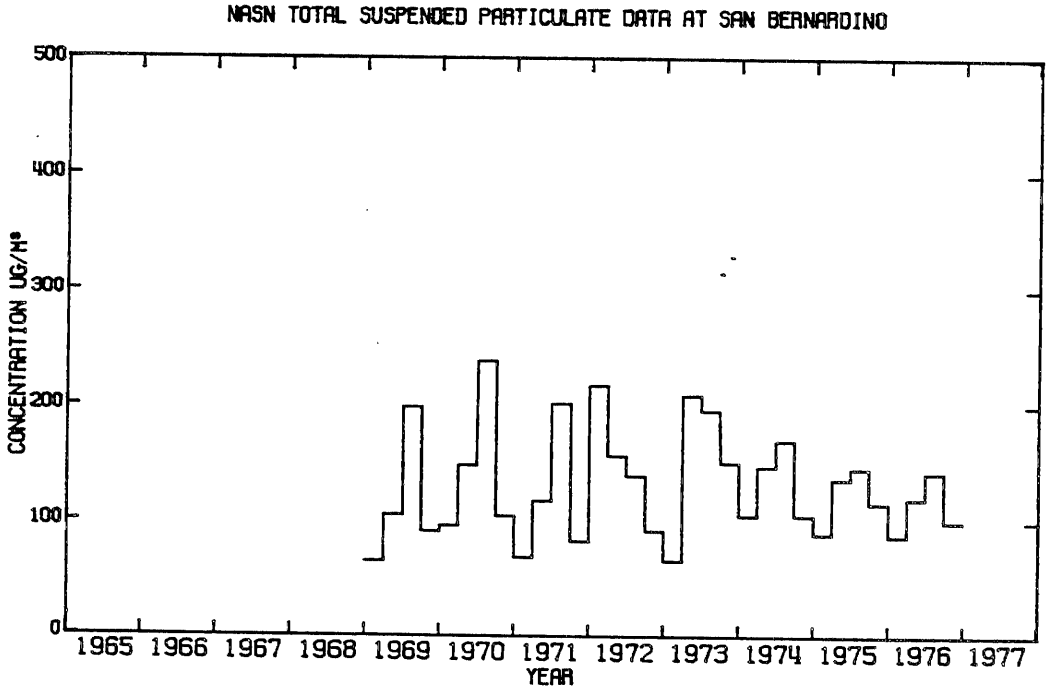



FIGURE A.12.14